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Attestation

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

99204567.4

PRIORITY DOCUMENT

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COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
THE HAGUE,
LA HAYE, LE

12/02/01





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Blatt 2 der B sch inigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.: 99204567.4
Demande n°:

Anmeldetag:
Date of filing: 28/12/99
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Anmelder:
Applicant(s):
Demandeur(s):
Monsell Technology Company bv
2132 MS Hoofddorp
NETHERLANDS

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Titre de l'invention:

Metallocene compounds and use thereof in catalyst systems for producing semicrystalline olefin polymers

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TC 5420

TITLE:

**METALLOCENE COMPOUNDS AND USE THEREOF IN CATALYST SYSTEMS
FOR PRODUCING SEMICRYSTALLINE OLEFIN POLYMERS**

The present invention relates to a new class of metallocene compounds, to catalysts containing them and to a process carried out in the presence of said catalysts for the preparation of isotactic polymers of alpha-olefins, particularly propylene polymers, having a low degree of crystallinity. The present invention also relates to the ligands for those metallocenes and to a convenient process for their preparation.

Products of the propylene homopolymerization can have varying degrees of crystallinity. The type and amount of crystallinity is largely dependent on the microstructure of the polypropylene. The polypropylene having predominantly isotactic or syndiotactic structure is partially crystalline, while the polypropylene having predominantly atactic structure is amorphous. Propylene polymers are also known which have a reduced degree of crystallinity and show elastomeric properties. U.S. patent No. 4,335,225, for instance, discloses a fractionable, elastic polypropylene, having an isotactic content of 55% or less, which contain a diethyl ether-soluble fraction with an isotactic crystalline content of about 0.5-5% by weight. This polypropylene is prepared with a catalyst based on tetraalkyl zirconium supported on a metal oxide. However, the elastomeric polypropylenes of this type, due to the fact that the catalyst systems which are used for their preparation have different catalytic sites, are endowed with a wide distribution of molecular weights which reflects negatively on their properties.

Metallocene catalysts have recently been used in the polymerization reaction of olefins. Operating in the presence of these catalysts, polymers characterized by a narrow molecular weight distribution and having structural characteristics of interest have been obtained. By polymerizing propylene in the presence of metallocene catalysts, amorphous or highly crystalline polypropylenes can be obtained depending on the metallocene used.

Certain metallocene catalysts are also known that can produce partially crystalline elastomeric polypropylene. International application WO 95/25757, for instance, describes unbridged metallocene catalysts that can produce isotactic-atactic stereoblock polypropylenes having elastomeric thermoplastic properties. Despite the homogeneity in molecular weight distribution, the tacticity distribution of these polymers is not homogeneous. Moreover, the activity is low.

U. Dietrich et al. In "J. Am. Chem. Soc. 1999, 121, 4348-4355" describe metallocene

(TCS420.EP)

catalysts that are able to produce thermoplastic elastic polypropylenes.

More recently, heterocyclic metallocene compounds have been used in the polymerization of alpha-olefins. In International application WO 98/22486 it is disclosed a class of metallocenes containing a cyclopentadienyl radical directly coordinating the central metal atom, to which are fused one or more rings containing at least one heteroatom. These metallocenes, in combination with a suitable cocatalyst, are used in the polymerization of olefins such as propylene. The working examples relate to the preparation of high stereoregular polypropylene.

It would be desirable to provide a novel class of metallocenes which, when used in catalysts for the polymerization of olefins, in particular propylene, are capable of yielding polymers endowed with high molecular weights, narrow molecular weight distribution and a reduced degree of crystallinity. It would be most desirable to provide metallocene catalysts that can produce those polymers with high activity, such that the amount of the catalyst remaining in the formed polymer is minimized.

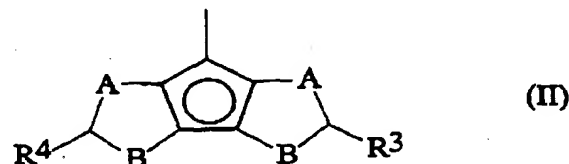
A novel class of metallocene compounds has now been unexpectedly found, which achieves the above and other results.

According to a first aspect the present invention provides a metallocene compound of the general formula (I):



wherein L is a divalent group bridging the moieties G and Z, selected from CR^1R^2 , SiR^1R^2 and $(\text{CR}^1\text{R}^2)_2$, R^1 and R^2 , same or different from each other, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom, which can form a ring having 3 to 8 atoms which can bear a substituent;

Z is a moiety of formula (II):

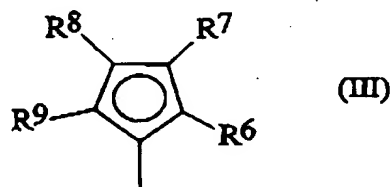


wherein R^3 and R^4 , same or different from each other, are selected from hydrogen, a

C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom, at least one of R^3 and R^4 being different from hydrogen;

A and B are selected from S, O or CR^5 , wherein R^5 is selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom, either A or B being different from CR^5 , and wherein the rings containing A and B have a double bond in the allowed position;

G is a moiety of formula (III):



wherein R^6 , R^7 , R^8 and R^9 , same or different from each other, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom, and R^6 and R^7 and/or R^8 and R^9 can form a ring comprising from 3 to 8 atoms, which can bear substituents, with the provisions that R^7 is different from R^8 and when R^7 is a tert-butyl radical, R^8 is not hydrogen;

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements (new IUPAC version),

X, same or different, is selected from a halogen atom, a R^{10} , OR^{10} , OSO_2CF_3 , $OCOR^{10}$, SR^{10} , NR^{10}_2 or PR^{10}_2 group, wherein the substituents R^{10} are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms;

p is an integer of from 0 to 3, being equal to the oxidation state of the metal M minus 2.

The transition metal M is preferably selected from titanium, zirconium and hafnium. The X substituents are preferably chlorine atoms or methyl groups. Preferably the bridging group L is a $=CMe_2$ or $=SiMe_2$ group. Preferably one of A and B is a sulfur atom and the other is a CH group. Preferably R^3 and R^4 are the same and are selected from a C_1 - C_{20} -alkyl group, which can contain a silicon atom. Most preferably R^3 and R^4 are a methyl or a trimethylsilyl radical.

Non-limiting examples of metallocene compounds according to the present invention are:

(TC5420.EP)

methylene(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dithiophene)zirconium dichloride and dimethyl;
methylene(3-ethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dithiophene)zirconium dichloride and dimethyl;
methylene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dithiophene)zirconium dichloride and dimethyl;
methylene(3-phenyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dithiophene)zirconium dichloride and dimethyl;
methylene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dithiophene)zirconium dichloride and dimethyl;
methylene(2,4-diethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dithiophene)zirconium dichloride and dimethyl;
methylene(2,4-diisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b'] dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b'] dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-triethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-triisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-
b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;
methylene(3-cyclohexyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dithiophene)zirconium dichloride and dimethyl;
methylene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)zirconium dichloride and dimethyl;
methylene-1-(indenyl)-7-(2,5-ditrimethylsilylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)zirconium dichloride and dimethyl;
methylene-1-(3-isopropyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)zirconium dichloride and dimethyl;
methylene-1-(3-ter-butyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)zirconium dichloride and dimethyl;

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methylene-1-(2,3-dimethyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride and dimethyl;

methylene-1-(3-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride and dimethyl;

methylene-1-(tetrahydroindenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride and dimethyl;

methylene(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(3-ethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(3-phenyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(2,4-diethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(2,4-diisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(2,3,5-triethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(2,3,5-triisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(3-cyclohexyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

(TC5420.EP)

methylene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene-1-(2-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene-1-(2,3-dimethyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene-1-(tetrahydroindenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(3-methyl-cyclopentadienyl)-4-(2,6-dimethylcyclopentadienyl-[2,1-b:4,3-b']dioxazol)zirconium dichloride and dimethyl;

methylene(3-isopropyl-cyclopentadienyl)-7-(2,5-ditrimethylsilylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;

methylene(3-methyl-cyclopentadienyl)-7-(2,5-ditrimethylsilylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)hafnium dichloride and dimethyl;

isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-ethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-phenyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-ditrimethylsilylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,4-diethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,4-diisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

(TCS420.BP)

isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-ditrimethylsilylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2-methyl-4-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,3,5-triethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,3,5-triisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-cyclohexyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-ditrimethylsilylcyclopentadienyl-[1,2-b:4,3-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-isopropyl-cyclopentadienyl)-4-(2,6-dimethylcyclopentadienyl-[2,1-b:3,4-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride and dimethyl;

isopropylidene-1-(3-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride and dimethyl;

isopropylidene-1-(2,3-dimethyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride and dimethyl;

isopropylidene-1-(3-isopropyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride and dimethyl;

isopropylidene-1-(3-tert-butyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride and dimethyl;

isopropylidene-1-(tetrahydroindenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-

(TC5420.EP)

b']dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-methyl-cyclopentadienyl)-4-(2,6-dimethylcyclopentadienyl-[2,1-b:3,4-b']
dithiophene)hafnium dichloride and dimethyl;
dimethylsilandiyl(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(3-ethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-
b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(3-phenyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-
b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,4-diethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-
b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,4-diisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-
b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-
b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,3,5-triethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-
b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,3,5-triisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-
[1,2-b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(3-cyclohexyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-
b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl(3-trimethylsilyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-
b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(3-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-

(TC5420.EP)

b']dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(2,3-dimethyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(3-ethyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(3-isopropyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(3-isopropyl-indenyl)-4-(2,6-dimethylcyclopentadienyl-[2,1-b:3,4-
b']dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(3-isopropyl-indenyl)-7-(2,5-ditrimethylsilylcyclopentadienyl-[1,2-
b:4,3-b']dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(3-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)hafnium dichloride and dimethyl;
dimethylsilandiyl-1-(3-tertbutyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(tetrahydroindenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dioxazol)zirconium dichloride and dimethyl;
isopropylidene(3-ethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dioxazol)zirconium dichloride and dimethyl;
isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b'] dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-phenyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']
dioxazol)zirconium dichloride and dimethyl;
isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dioxazol)zirconium dichloride and dimethyl;
isopropylidene(2,4-diethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-
b']dioxazol)zirconium dichloride and dimethyl;
isopropylidene(2,4-diisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-

(TCS420.EP)

b:4,3-b']dioxazol)zirconium dichloride and dimethyl;
isopropylidene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene(2,3,5-triethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene(2,3,5-triisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene(3-cyclohexyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene-1-(3-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene-1-(3-ethyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene-1-(3-isopropyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene-1-(3-tert-butyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene-1-(tetrahydroindenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene-1-(tetrahydroindenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)hafnium dichloride and dimethyl;
dimethylsilandiyl(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(3-ethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-

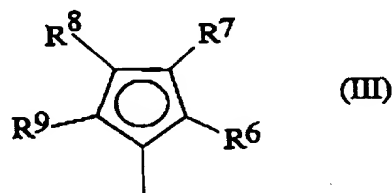
(ICS420.EP)

b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(3-phenyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,4-diethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,4-diisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,3,5-triethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(2,3,5-trisopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(3-cyclohexyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(3-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(2,3-dimethyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(3-isopropyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
dimethylsilandiyl-1-(tetrahydroindenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dioxazol)zirconium dichloride and dimethyl;
isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-

(TC5420.EP)

b']-dithiophene)zirconium dichloride;
 isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(3-isopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride;
 dimethylsilandiyl-1-(indenyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)hafnium dichloride;
 isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(3-isopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride.

A particular interesting class of bridged metallocenes of formula (I) according to the present invention are those wherein G is a moiety of formula (III):



wherein R^6 and R^9 , same or different from each other, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom,

R^7 is selected from a C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or a $QR^{11}R^{12}R^{13}$ group, wherein Q is selected from C, Si, Ge;

(TCS420.EP)

R^{11} , R^{12} and R^{13} , same or different from each other, are hydrogen, C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radicals, optionally containing a heteroatom, with the proviso that when Q is a carbon atom, at least one of R^{11} , R^{12} and R^{13} is a hydrogen atom, and

R^8 is hydrogen.

Particularly preferred metallocenes of the above mentioned class are those wherein R^7 is selected from a phenyl group, a $CHR^{11}R^{12}$ group and a $SiR^{11}R^{12}R^{13}$ group, R^{11} , R^{12} and R^{13} being hydrogen or C_1 - C_{20} -alkyl groups.

Most preferred are those metallocene wherein $QR^{11}R^{12}R^{13}$ is an isopropyl or a trimethylsilyl group.

Non-limiting examples of this class of metallocenes are:

isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

dimethylsilyl(3-trimethylsilyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(2-methyl-4-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(3-isopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride;

isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(3-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

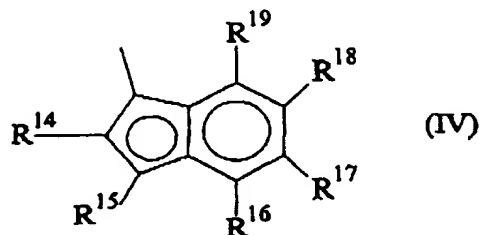
isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-

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b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl)-cyclopentadienyl-
 [1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 dimethylsilandiyl(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-
 b:4,3-b']-dithiophene)zirconium dichloride; and
 isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-
 dithiophene)hafnium dichloride.

Another advantageous class of bridged metallocenes of formula (I) are those wherein G is a moiety of formula (IV):



wherein R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸ and R¹⁹, same or different from each other, are selected from hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms, and any of two adjacent R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸ and R¹⁹ can form a ring comprising 4 to 8 atoms which can bear substituents and the benzene ring can be perhydrated.

Preferably R¹⁵, R¹⁶, R¹⁷, R¹⁸ and R¹⁹ are hydrogen and R¹⁴ is a C₁-C₂₀-alkyl group such as a methyl or ethyl group.

Non-limiting examples of metallocenes belonging to this class are:

dimethylsilandiyl-1-(indenyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-
 dithiophene)zirconium dichloride;
 dimethylsilandiyl-1-(2-methyl-indenyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-
 dithiophene)zirconium dichloride.

According to another aspect of the present invention there is provided a class of ligands of formula (V):

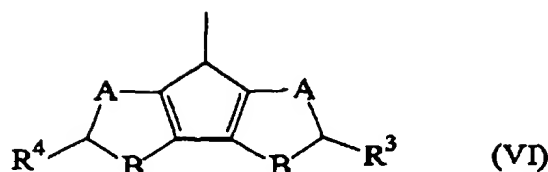


wherein L is defined as described above;

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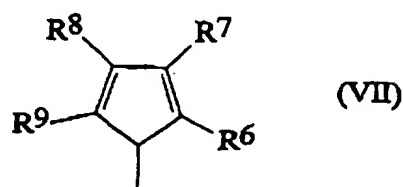
Z' is a moiety of formula (VI):



and its double bond isomers;

wherein A, B, R³ and R⁴ are defined as described above;

G' is a moiety of formula (VII):



and its double bond isomers;

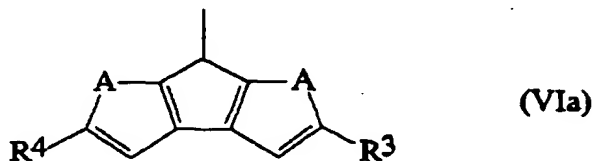
wherein R⁶, R⁷, R⁸ and R⁹ have the meaning as defined above.

According to a further aspect of the present invention there is provided a process for the preparation of a ligand of formula (V):



wherein G' and L are defined as described above;

Z' is a moiety of formula (VIa):



and its double bond isomers;

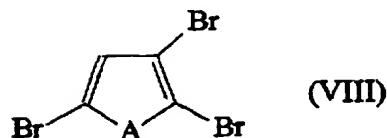
wherein A is sulfur or oxygen, R³ and R⁴ are the same and are selected from a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing a heteroatom;

comprising the following steps:

a) contacting a compound of formula (VIII):

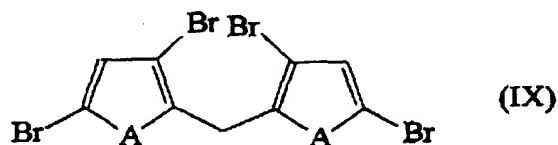
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with a base selected from an organic lithium compound, sodium or potassium; and subsequent treatment with a formic ester, wherein the molar ratio between said ester and the compound of formula (VIII) is at least 1:2, and subsequently

- b) treating with a reducing agent in order to obtain a compound of formula (IX):



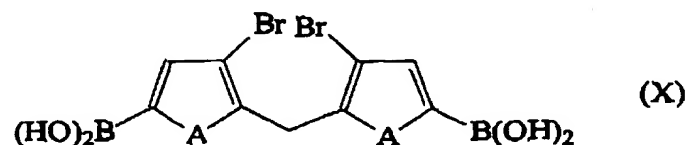
- c) contacting with a base selected from an organic lithium compound, sodium or potassium;

and subsequent treatment with an alkylating agent,

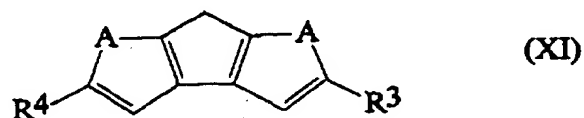
- d) contacting with a base selected from an organic lithium compound, sodium or potassium;

and subsequent treatment with a coupling agent; or contacting the above defined compound of formula (VIII) with a base selected from an organic lithium compound, sodium or potassium;

followed by treating with an ester of boric acid and a protonating agent in order to obtain the compound of formula (X):

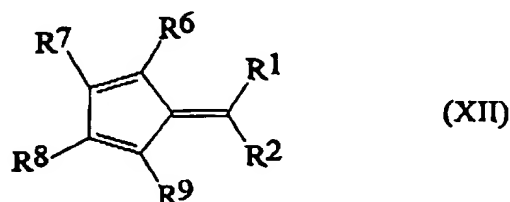


and subsequently contacting with a mixture of an alkylating agent in the presence of an transition metal complex compound followed by above step d), in order to obtain the compound of formula (XI);

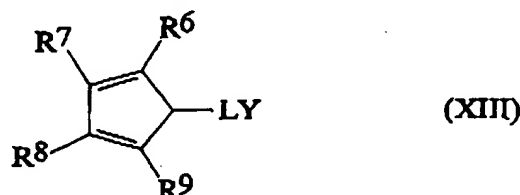


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- e) contacting the compound of the formula (XI) with a base selected from the group consisting of metallic sodium and potassium, sodium and potassium hydroxide and an organic lithium compound, wherein the molar ratio between the compound of the formulae (XI) and said base is at least 1;
- f) when L is $\text{CR}^{11}\text{R}^{12}$ contacting the corresponding anionic moiety of the formula (XI) with a compound of the general formula (XII):



wherein R^1 , R^2 , R^6 , R^7 , R^8 and R^9 have the meaning as defined above;
 or, when L is a SiR^1R^2 or $(\text{CR}^1\text{R}^2)_2$, contacting the corresponding anionic compounds of the formula (XI) with a compound of general formula (XIII):



wherein R^6 , R^7 , R^8 and R^9 are defined as above and Y is a halogen radical selected from the group consisting of fluoride, chloride, bromide and iodide;

- g) treating with a protonating agent.

Preferably the reducing agent is a mixture of $\text{AlCl}_3/\text{LiAlH}_4$ or a mixture of triethylsilane (Et_3SiH) and CF_3COOH . Preferably the base is butyllithium. Preferably the organic acid ester is an ester of formic acid. Preferably the alkylation agent is selected from dimethylsulphate (Me_2SO_4), trimethylchlorosilane (Me_3SiCl) and a mixture of compounds of formulae $\text{R}^3\text{Y}'$ and $\text{R}^4\text{Y}'$, wherein R^3 and R^4 are defined as above and Y' is selected from chloride, bromide and iodide. Most preferably the halogen radical is chloride or bromide. Preferably the coupling agent is selected from the group consisting of copper chloride, iodine and Mg/Pd . Preferably the transition metal complex compound is $\text{PdCl}_2(\text{dppf})$. Preferably Y is a chloride radical. Preferably the base used for the preparation of the corresponding anionic

form of the compound of formula (VIII) is butyllithium. Preferably the compound of formula (XII) is selected from 3,6,6-trimethylfulvene and 3-isopropyl-6,6-dimethylfulvene. Non-limiting examples of compounds of formula (XIII) are (3-methyl-cyclopentadienyl)dimethylchlorosilane, (3-isopropyl-cyclopentadienyl)dimethyl chlorosilane, 1-(3-methyl-cyclopentadienyl)-1,1-dimethyl-2,2-dimethyl-2-chloro-ethane and 1-(3-isopropyl-cyclopentadienyl)-1,1-dimethyl-2,2-dimethyl-2-chloro-ethane.

Compounds of formula (V) can suitably be used as intermediates for the preparation of metallocenes of formula (I).

Therefore, a still further aspect of the present invention is a process for the preparation of a metallocene compound of formula (I), obtainable by contacting the ligand of general formula (V), with a compound capable of forming the corresponding dianionic compound thereof and thereafter with a compound of general formula MX_{p+2} , wherein M, X and p are defined as above.

The compound able to form said corresponding dianionic compound is selected from the group consisting of hydroxides of alkali- and earth-alkali metals, metallic sodium and potassium, and organometallic lithium salts.

Preferably, the compound able to form said corresponding dianionic compound is butyllithium.

Non-limiting examples of compounds of formula MX_{p+2} are titanium-, zirconium- and hafniumtetrachloride.

The metallocene compounds of formula (I) can be prepared by first reacting the ligands of formula (V), prepared as described above, with a compound able to form a delocalized anion on the cyclopentadienyl rings, and thereafter with a compound of formula MX_{p+2} , wherein M and the substituents X are defined as above.

More specifically, said ligands are dissolved in an aprotic polar solvent and to the obtained solution is added a solution of an organic lithium compound in an apolar solvent. The thus obtained anionic form is separated, dissolved in an aprotic polar solvent and thereafter added to a suspension of the compound MX_{p+2} in an aprotic polar solvent. At the end of the reaction, the solid product obtained is separated from the reaction mixture by techniques commonly used in the state of the art. Non limiting examples of aprotic polar solvents suitable for the

above reported processes are tetrahydrofuran, dimethoxyethane, diethylether, toluene and dichloromethane. Non limiting examples of apolar solvents suitable for the above process are pentane, hexane and benzene.

During the whole process, the temperature is generally kept between -180°C and 80°C , preferably between -20°C and 40°C .

In the case in which at least one substituent X in the metallocene compound of the formula (I) which is to be prepared is other than a halogen, it is necessary to substitute at least one substituent X in the metallocene obtained by at least one substituent X other than a halogen.

The reaction of substituting substituents X by substituents X other than a halogen is carried out using generally applied methods. For example, if the desired substituents X are alkyl groups, the metallocenes can be made to react with alkylmagnesium halides (Grignard reagents) or with alkyllithium compounds.

According to a still further aspect of the present invention there is provided a catalyst for the polymerization of α -olefins, obtainable by contacting:

- (A) a metallocene compound of formula (I) according to the present invention, and
- (B) an alumoxane and/or a compound capable of forming an alkyl metallocene cation.

The alumoxane used as component (B) can be obtained by reacting water with an organo-aluminium compound of formula AlR^{20} , or $\text{Al}_2\text{R}^{20}_2$, wherein the R^{20} substituents, same or different from each other, are defined as R^1 . In this reaction the molar ratio of Al/water is comprised between 1:1 and 100:1.

Non-limiting examples of aluminium compounds of the formula AlR^{20} , or $\text{Al}_2\text{R}^{20}_2$ are:

$\text{Al}(\text{Me})_3$, $\text{Al}(\text{Et})_3$, $\text{AlH}(\text{Et})_2$, $\text{Al}(\text{iBu})_3$, $\text{AlH}(\text{iBu})_2$, $\text{Al}(\text{iHex})_3$, $\text{Al}(\text{iOct})_3$, $\text{AlH}(\text{iOct})_2$, $\text{Al}(\text{C}_6\text{H}_5)_3$, $\text{Al}(\text{CH}_2\text{-CH}(\text{Me})\text{CH}(\text{Me})_2)_3$, $\text{Al}(\text{CH}_2\text{C}_6\text{H}_5)_3$, $\text{Al}(\text{CH}_2\text{CMe}_3)_3$, $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$, $\text{Al}(\text{Me})_2\text{iBu}$, $\text{Al}(\text{Me})_2\text{Et}$, $\text{AlMe}(\text{Et})_2$, $\text{AlMe}(\text{iBu})_2$, $\text{Al}(\text{Me})_2\text{iBu}$, $\text{Al}(\text{Me})_2\text{Cl}$, $\text{Al}(\text{Et})_2\text{Cl}$, AlEtCl_2 and $\text{Al}_2(\text{Et})_3\text{Cl}_3$, wherein Me = methyl, Et = ethyl, iBu = isobutyl, iHex = isohexyl, iOct = 2,4,4-trimethyl-pentyl.

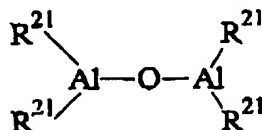
Amongst the above aluminium compounds, trimethylaluminium (TMA), triisobutylaluminium (TIBAL) and tris(2,4,4-trimethyl-pentyl)aluminium (TIOA) are preferred.

The alumoxanes used in the catalyst according to the invention are considered to be linear,

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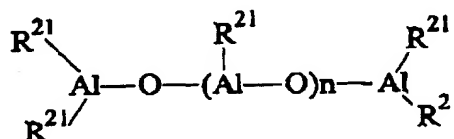
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branched or cyclic compounds containing at least one group of the type:

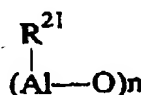


wherein the substituents R^{21} , same or different, are C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radicals, optionally containing hydrogen atoms, silicon or germanium atoms, or a $-\text{O}-\text{Al}(\text{R}^{21})_2$ group and, if appropriate, some substituents R^{21} can be halogen atoms.

In particular, alumoxanes of the formula:



can be used in the case of linear compounds, wherein n is 0 or an integer of from 1 to 40 and the substituents R^{21} are defined as above, or alumoxanes of the formula:



can be used in the case of cyclic compounds, wherein n is an integer of from 2 to 40 and the R^{21} substituents are defined as above.

The substituents R^{17} are preferably ethyl, isobutyl or 2,4,4-trimethyl-pentyl groups. Examples of alumoxanes suitable for use according to the present invention are methylalumoxane (MAO), isobutylalumoxane (TIBAO) and 2,4,4-trimethyl-pentylalumoxane (TIOAO).

The molar ratio between the aluminium and the metal of the metallocene compound is in general comprised between 10:1 and 20000:1, and preferably between 100:1 and 5000:1.

Non-limiting examples of compounds able to form an alkylmetallocene cation are compounds of the formula D^+E^- , wherein D^+ is a Brønsted acid, able to donate a proton and to react irreversibly with a substituent X of the compound of the formula (I), and E^- is a compatible anion which does not coordinate and which is able to stabilize the active catalytic species which results from the reaction of the two compounds and which is sufficiently labile to be displaceable by an olefin substrate. Preferably, the anion E^- consists of one or more boron

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atoms. More preferably, the anion E^- is an anion of the formula $BAr_n^{(n)}$, wherein the substituents Ar which can be identical or different are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred. Moreover, compounds of the formula BAr_n can conveniently be used. Compounds of this type are described, for example, in the published International patent application WO 92/00333. Further, compounds of the formula $RM-O-MR$, R being an alkyl or aryl group, and M is selected from an element of the Group 13 of the Periodic Table of the Elements (new IUPAC version). Compounds of this type are described, for example, in the International patent application WO 99/40129.

The catalysts of the present invention can also be used on supports. This is achieved by depositing the metallocene compound (A) or the product of the reaction thereof with the component (B), or the component (B) and then the metallocene compound (A) on supports such as, for example, silica, alumina, magnesium halides, styrene/divinylbenzene copolymers, polyethylene or polypropylene.

A suitable class of supports which can be used is that constituted by porous organic supports functionalized with groups having active hydrogen atoms. Particularly suitable are those in which the organic support is a partially crosslinked styrene polymer. Supports of this type are described in European application EP-633 272.

Another class of inert supports particularly suitable for use according to the invention is that of the olefin, particularly propylene, porous prepolymers described in International application WO 95/26369.

A further suitable class of inert supports for use according to the invention is that of the porous magnesium halides such as those described in International application WO 95/32995. The solid compound thus obtained, in combination with the further addition of the alkylaluminium compound either as such or prereacted with water if necessary, can be usefully employed in the gas-phase polymerization.

According to a still further aspect of the present invention it is provided a process for the preparation of polymers of alpha-olefins in the presence of a catalyst comprising the product obtainable by contacting:

(A) a metallocene compound of the general formula (I):

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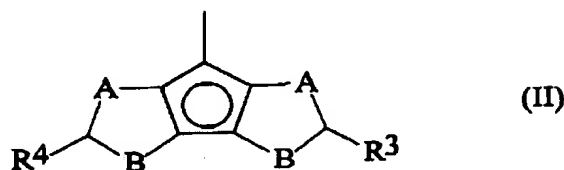
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LGZMXp (I)

wherein L, G, M, X and p are defined as described above;

Z is a moiety of formula (II):



wherein A and B are defined as described above;

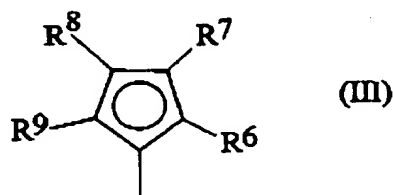
R^3 and R^4 , same or different from each other, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom,

and

(B) an alumoxane and/or a compound capable of forming an alkyl metallocene cation.

The transition metal M is preferably selected from titanium, zirconium and hafnium. Most preferably zirconium is used. The X substituents are preferably chlorine atoms or methyl groups. Preferably one of A is a sulfur atom and the other is a CH group. Preferably R^3 , which is the same as R^4 , is selected from hydrogen and a C_1 - C_{20} -alkyl group, which can contain a silicon atom. Most preferably R^3 and R^4 are a methyl or a trimethylsilyl radical. Preferably the bridging group L is $=CMe_2$ or $=SiMe_2$.

Particularly good results are obtained when the process of the present invention is carried out in the presence of a metallocene of formula (III), wherein G is a moiety of formula (III):



wherein R^6 and R^9 , same or different from each other, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom,

R^7 is selected from a C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or a $QR^{11}R^{12}R^{13}$ group, wherein Q is selected from C, Si, Ge,

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R^{11} , R^{12} and R^{13} , same or different from each other, are hydrogen, C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radicals, optionally containing a heteroatom, with the proviso that when Q is a carbon atom, at least one of R^{11} , R^{12} and R^{13} is a hydrogen atom; and

R^8 is hydrogen.

Preferably R^7 is selected from phenyl, a $CHR^{11}R^{12}$ and a $SiR^{11}R^{12}R^{13}$ group, wherein R^{11} , R^{12} and R^{13} are hydrogen or C_1 - C_{20} -alkyl groups. Most preferably $QR^{11}R^{12}R^{13}$ is an isopropyl or a trimethylsilyl group.

Non-limiting examples of this class of metallocenes used in the process of the present invention are

isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

dimethylsilyl(3-trimethylsilyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(2-methyl-4-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(3-isopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride;

isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(3-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

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isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl)-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
dimethylsilandiyl(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
isopropylidene(3-isopropylcyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and
isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)hafnium dichloride.

Particularly good results are also obtained when the process of the present invention is carried out in the presence of a particular class of metallocenes of formula (I), wherein G is a moiety of formula (IV) as mentioned above.

Non-limiting examples of metallocenes used in the process of the present invention are:

dimethylsilandiyl-1-(indenyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
dimethylsilandiyl-1-(2-methyl-indenyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
dimethylsilandiyl-1-(indenyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride.

The process for the polymerization of olefins according to the invention can be carried out in the liquid phase in the presence or absence of an inert hydrocarbon solvent, or in the gas phase. The hydrocarbon solvent can either be aromatic such as toluene, or aliphatic such as propane, hexane, heptane, isobutane or cyclohexane.

The polymerization temperature is generally comprised between -100°C and +100°C and, particularly between 10°C and +90°C. The polymerization pressure is generally comprised between 0,5 and 100 bar.

The lower the polymerization temperature, the higher are the resulting molecular weights of the polymers obtained.

The polymerization yields depend on the purity of the metallocene compound of the catalyst. The metallocene compounds obtained by the process of the invention can therefore be used as such or can be subjected to purification treatments.

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The components of the catalyst can be brought into contact with each other before the polymerization. The pre-contact concentrations are generally between 0.1 and 10^{-6} mol/l for the metallocene component (A), while they are generally between 2 and 10^{-8} mol/l for the component (B). The pre-contact is generally effected in the presence of a hydrocarbon solvent and, if appropriate, of small quantities of monomer. In the pre-contact it is also possible to use a non-polymerizable olefin such as isobutene, 2-butene and the like.

The propylene polymers obtainable with the process of the present invention may have a varying content of isotactic sequences.

In the structure of the above polymers of propylene it is observed that the isotactic triads (mm) satisfy the relation:

$$30 < mm < 85 \text{ and}$$

$$\text{preferably } 40 < mm < 80.$$

The tacticity of the polymeric chain, i.e. the distribution of the relative configuration of the tertiary carbons, is determined by ^{13}C -NMR analysis.

The melting enthalpy is generally lower than 70 J/g.

The molecular weights of the above said propylene polymers can be quite high. Thus, the intrinsic viscosity can reach values of greater than 0.5 dl/g, even greater than 1 dl/g.

Further, the molecular weights of the propylene polymers are distributed over relatively limited ranges. The molecular weight distribution can be represented by the ratio M_w/M_n which, for the present polymers, is generally lower than 4, preferably lower than 3.5 and, more preferably, lower than 3.

The molecular weight distribution can be varied by using mixtures of different metallocene compounds or by carrying out the polymerization in several stages which differ as to the polymerization temperature and/or the concentrations of the molecular weight regulators.

The polymerization reaction according to the invention can be carried out in the presence of ethylene or of a $\text{C}_4\text{-C}_{10}$ alpha-olefin comonomer. Thus a further aspect of the present invention is a propylene copolymer containing from 0.1 to 20% by moles of units deriving from an olefin of formula $\text{CH}_2=\text{CHR}$, R being hydrogen, a $\text{C}_2\text{-C}_{20}$ -alkyl or a $\text{C}_6\text{-C}_{12}$ -aryl group, said propylene copolymer having the following characteristics:

- melting enthalpy < 70 J/g;

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The proton and carbon spectra of ligands and metallocenes were obtained using a Bruker DPX 200 spectrometer operating in the Fourier transform mode at room temperature at 200.13 MHz and 50.32 MHz respectively. The samples were dissolved in CDCl_3 or CD_2Cl_2 . As reference the residual peak of CHCl_3 or CHDCl_2 in the ^1H spectra (7.25 ppm and 5.35 ppm, respectively) and the peak of the solvent in the ^{13}C spectra (77.00 ppm for CDCl_3) were used. Proton spectra were acquired with a 15° pulse and 2 seconds of delay between pulses; 32 transients were stored for each spectrum. The carbon spectra were acquired with a 45° pulse and 6 seconds of delay between pulses; about 512 transients were stored for each spectrum. All NMR solvents were dried over P_2O_5 and distilled before use. Preparation of the samples was carried out under nitrogen using standard inert atmosphere techniques.

The proton and carbon spectra of polymers were obtained using a Bruker DPX 400 spectrometer operating in the Fourier transform mode at 120°C at 400.13 MHz and 100.61 MHz respectively. The samples were dissolved in $\text{C}_2\text{D}_2\text{Cl}_4$. As reference the residual peak of C_2DHCl_4 in the ^1H spectra (5.95 ppm) and the peak of the mmmmm pentad in the ^{13}C spectra (21.8 ppm) were used. Proton spectra were acquired with a 45° pulse and 5 seconds of delay between pulses; 256 transients were stored for each spectrum. The carbon spectra were acquired with a 90° pulse and 12 seconds (15 seconds for ethylene based polymers) of delay between pulses and CPD (waltz 16) to remove ^1H - ^{13}C couplings. About 3000 transients were stored for each spectrum.

GC-MS analyses were carried out on a HP 5890 – serie 2 gas-chromatograph and a HP 5989B quadrupole mass spectrometer.

The intrinsic viscosity (I.V.) was measured in tetrahydronaphtalene solution (THN) obtained by dissolving the polymer at 135°C for 1 h.

The melting points of the polymers (T_m) were measured by Differential Scanning Calorimetry (D.S.C.) on an instrument Perkin Elmer DSC-7, according to the following method. The instrument was calibrated with indium and tin standards. Weighted sample (5-10 mg) obtained from the polymerization was sealed into aluminum pans and heated at 200°C with a scanning speed corresponding to $20^\circ\text{C}/\text{minute}$. The sample was kept at 200°C for 5 minutes to allow a complete melting of all the crystallites. Successively, after cooling to 0°C with a

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scanning speed corresponding to 20°C/minute, the peak temperature was assumed as crystallization temperature (T_c). After standing 5 minutes at 0°C, the sample was heated for the second time at 200°C with a scanning speed corresponding to 10°C/min. In this second heating run, the peak temperature was assumed as melting temperature (T_m) and the area as global melting enthalpy (ΔH_f).

The distribution of molecular weights was determined by GPC carried out on an instrument WATERS 200 in orthodichlorobenzene (stabilized with BHT, 0.1 wt.%) at 135°C.

A commercial (Witco) 10% toluene solution of methylalumoxane (MAO) was dried in vacuum until a solid, glassy material was obtained, which was finely crushed and further treated in vacuum until all volatiles were removed (4-6 h, 0.1 mmHg, 50°C) to leave a white, free-flowing powder.

The following abbreviations are used:

THF = tetrahydrofuran

Et₂O = diethyl ether

Me₂SiCl₂ = dichlorodimethylsilane

Me₃SiCl = chlorotrimethylsilane

CuCl₂ = copper (II) chloride

B(OMe)₃ = trimethyl borate

DMF = N,N-dimethylformamide

n-BuLi = normal butyllithium

Dppf = diphenylphosphinoferrocene

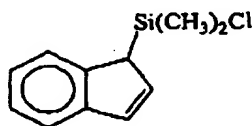
TMEDA = N,N,N',N'-tetramethylethylenediamine

ZrCl₄ = zirconium tetrachloride

HfCl₄ = hafnium chloride

PREPARATION OF THE LIGAND PRECURSORS

Synthesis of chloro(1-indenyl)dimethylsilane

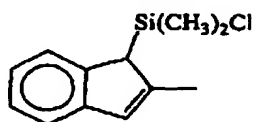


37.5 mL of a 2.5 M solution of *n*-BuLi in hexane (93.75 mmol, *n*-BuLi:indene = 1.1:1) was

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added dropwise to a solution of indene (purity 90 %, 11 g, 85.23 mmol) in 60 mL of Et₂O, previously cooled to -78°C. At the end of the addition, the yellow slurry was allowed to reach room temperature and stirred for 4 hours to give an orange solution. The solvents were evaporated under reduced pressure to give a yellow solid, which was taken up in 75 mL of hexane; the milky suspension was stirred for few minutes and the lithium salt of indene (white precipitate) was filtered and washed with hexane (3×20 mL). The solid was again slurried in hexane (40 mL) and added to a stirred solution of Me₂SiCl₂ (15.5 mL, 127.84 mmol, Me₂SiCl₂/IndLi = 1.5:1) in 50 mL of hexane, previously cooled to -78 °C. At the end of the addition, the mixture was allowed to reach room temperature and stirred overnight. The suspension was then filtered, and the filtrate brought to dryness in vacuum to yield a light yellow oil (16.5 g) of (1-Ind)SiMe₂Cl free from its vinylic isomer (yield 89 %). The title compound was analyzed by ¹H NMR spectroscopy.

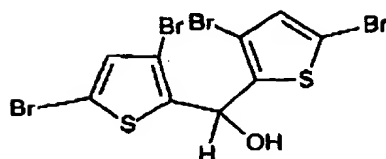
Synthesis of chloro(2-Me-1-indenyl)dimethylsilane



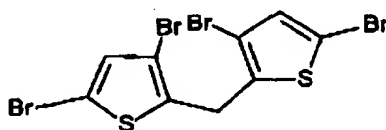
4.56 mL of a 2.5 M solution of *n*-BuLi in hexane (11.4 mmol) was added dropwise to a solution of 2-methylindene (Boulder Scientific Company, 1.45 g, 11.1 mmol) in 11 mL of Et₂O, previously cooled to -78°C. At the end of the addition, the mixture was allowed to reach room temperature and stirred for 4 hours to give a yellow suspension. The solvents were evaporated under reduced pressure to give a yellow solid, which was taken up in hexane; the milky suspension was stirred for few minutes and the lithium salt of 2-methylindene (white precipitate) was filtered and washed with hexane. The solid was again slurried in hexane and added to a stirred solution of Me₂SiCl₂ (1.85 mL, 16.6 mmol, Me₂SiCl₂/IndLi = 1.5:1) in 7 mL of hexane, previously cooled to -78 °C. At the end of the addition, the white thick slurry was allowed to reach room temperature and stirred overnight. The suspension was then filtered and the filtrate brought to dryness in vacuum to yield a light yellow oil (1.98 g) of (2-Me-1-Ind)SiMe₂Cl (yield 80 %). The title compound was analyzed by ¹H NMR spectroscopy.

Synthesis of bis(3,5-dibromo-2-thienyl)methane 1 (or 3,3',5,5'-tetrabromo-2,2'-

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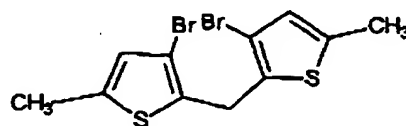
dithienyl carbin 1)

A solution of 31.35 g of 2,3,5-tribromothiophene (Lancaster, 98%, MW = 320.84, 95.75 mmol) in 70 mL of ether was cooled to -78°C and added dropwise of 38.3 mL of a 2.5 M *n*-BuLi solution in hexane (95.75 mmol). The resulting mixture was allowed to warm up to room temperature, stirred in additional 1 h and then added at $0 \div -10^{\circ}\text{C}$ to a solution of 3.86 mL of ethylformate (Aldrich, 97%, MW = 74.08, $d = 0.917$, 46.35 mmol) in 20 mL of hexane, previously cooled to $0 \div -10^{\circ}\text{C}$. At the end of the addition (~ 20 min) the reaction mixture was allowed to warm up to room temperature and then refluxed for 1 h. The resulting mixture was quenched with 7.5 mL of water, the organic layer was separated, dried by magnesium sulphate and the solvents evaporated giving 23.2 g of a light brown solid, which was analyzed by ^1H NMR, ^{13}C NMR, GC-MS. Purity = 93.0%. Isolated yield towards ethylformate = 90.9%. The title compound was analyzed by ^1H NMR and ^{13}C NMR spectroscopy.

Synthesis of 3,3',5,5'-tetrabromo-2,2'-dithienylmethane

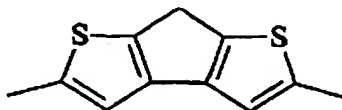
Trifluoroacetic acid (0.25 mL, Aldrich, 99%, MW = 114.02, $d = 1.48$, 3.24 mmol) was added at room temperature to a solution of 1.75 g of bis(3,5-dibromo-2-thienyl)methanol (93.0%, MW = 511.90, 3.18 mmol) in 15 mL of methylene chloride containing 0.50 mL of triethylsilane (Aldrich, 99%, MW = 116.28, $d = 0.728$, 3.13 mmol). The resulting red solution was stirred for 1 h at room temperature, neutralized with solid potassium carbonate (0.4 g, MW = 138.21, 2.89 mmol), filtered and evaporated to leave a light red solid. Yield of crude product = 100%.

The title compound was analyzed by ^1H NMR and ^{13}C NMR spectroscopy.

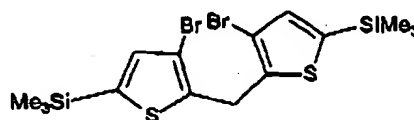
Synthesis of 3,3'-dibromo-5,5'-dimethyl-2,2'-dithienylmethane

A precooled (-20°C) 2.5 M solution of *n*-BuLi in hexane (41.1 mL, 102.75 mmol) was added at -20°C to a solution of 25.48 g of 3,3',5,5'-tetrabromo-2,2'-dithienylmethane (MW = 495.90, 51.38 mmol) in 100 mL of Et_2O . After 30 min stirring at -20°C , a precooled (-20°C) ethereal (10 mL) solution of dimethyl sulphate (Aldrich, 9.72 mL, MW = 126.13, $d = 1.333$, 102.75 mmol) was added. The resulting black suspension was stirred for 45 min at -20°C ; the cooling bath was then removed and the flow of nitrogen stopped. A 4 N solution of sodium hydroxide (2.5 mL, 10 mmol) was added and the mixture vigorously stirred for 2 h at room temperature. The resulting reaction mixture was dried by magnesium sulphate, filtered, the residue on the frit washed twice with ether (to recover all the product) and the filtrate concentrated under reduced pressure at 40°C for 2 h giving 17.8 g of a brown solid. Purity = 87.8% (by GC-MS). Yield of pure product = 83.1% (raw yield = 94.6%).

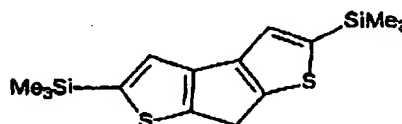
The title compound was analyzed by ^1H NMR, ^{13}C NMR and MS spectroscopy.

Synthesis of 2,5-dimethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene (or 2,5-dimethyl-7H-thieno[3',2':3,4]cyclopenta[b]thiophene)

A solution of 0.1 mol of 3,3'-dibromo-5,5'-dimethyl-2,2'-dithienylmethane in 200 mL ether was treated with 0.23 mol of *n*-BuLi at -70°C . At the end of the addition, the reaction mixture was stirred for additional 30 min at the same temperature. Then 0.265 mol of CuCl_2 was added quickly. The resulting mixture was allowed to warm up to room temperature and stirred for 12 h. The final suspension was poured into water, the organic layer was separated and concentrated. The residue was recrystallized from ether. Yield 25%. The title compound was analyzed by ^1H NMR and ^{13}C NMR spectroscopy.

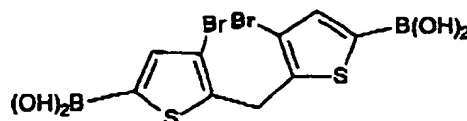
Synthesis of 3,3'-dibromo-5,5'-ditrimethylsilyl-2,2'-dithienylmethane

A 2.18 M solution of *n*-BuLi (65 mL, 141.7 mmol) was added at -70°C to a solution of 34.8 g of 3,3',5,5'-tetrabromo-2,2'-dithienylmethane (70.2 mmol) in 150 mL of ether. The mixture was stirred for 30 min at the same temperature and then added of 35.5 mL of Me_3SiCl (280 mmol) in 65 mL of ether. The resulting mixture was allowed to warm up to room temperature, the LiCl was filtered, and the mother solution was evaporated to give an oil which represented the target compound in at least 95% purity. To this oil 50 mL of hexane was added and the resulting solution kept at -30°C for 10 h. Big crystals were isolated, washed with cooled hexane and dried. Yield of recrystallized product 60%. The title compound was characterized by ^1H -NMR and ^{13}C -NMR spectroscopy.

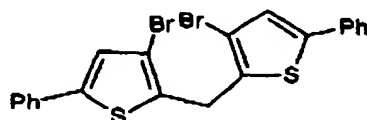
Synthesis of 2,5-ditrimethylsilyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene (or 2,5-dimethyltrimethylsilyl-7H-thieno[3',2':3,4]cyclopenta[b]thiophene)

A solution of 0.1 mol of 3,3'-dibromo-5,5'-ditrimethylsilyl-2,2'-dithienylmethane in 200 mL ether was treated with 0.23 mol of *n*-BuLi at -70°C . At the end of the addition, the reaction mixture was stirred for additional 30 min at the same temperature. Then 0.265 mol of CuCl_2 was added quickly. The resulting mixture was allowed to warm up to room temperature and stirred overnight. The resulting suspension was poured into water, the organic phase was separated and concentrated. The residue was passed through a column packed with SiO_2 using hexane or a mixture hexane/ether as eluent. The resulting solution was evaporated giving a crystalline or oily-crystalline solid which represented the desired product. Yield 50-60%. The crude product can be further purified in ether by filtration at 0°C or by recrystallization from pentane. The title compound was characterized by ^1H -NMR and ^{13}C -NMR spectroscopy.

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Synthesis of 3,3'-dibromo-5,5'-dihydroxyboryl-2,2'-dithienylmethane

A 1.6 N solution of *n*-BuLi (100 ml, 160mmol) was added to a solution of 39.6 g of 3,3',5,5'-tetrabromo-2,2'-dithienylmethane (79.8 mmol) in 150 mL ether at -70°C . The mixture was stirred for 30 min at the same temperature and then added of 23.3 g of $\text{B}(\text{OMe})_3$ (220mmol) in 100 mL of ether. The reaction mixture was allowed to warm up to room temperature. The resulting suspension was treated with 100 mL of a 10% aqueous HCl solution, the organic layer was separated, washed twice with 50 mL of a 10% aqueous Na_2CO_3 solution, evaporated and dried. The resulting solid which represented the crude di-boronic acid was used in the next step without further purification. The title compound was characterized by ^1H -NMR and ^{13}C -NMR spectroscopy.

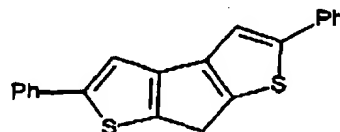
Synthesis of 3,3'-dibromo-5,5'-diphenyl-2,2'-dithienylmethane

1.81 g of 3,3'-dibromo-5,5'-dihydroxyboryl-2,2'-dithienylmethane (3.76 mmol), 1.40 g of PhI (6.84mmol), 0.15 g of $\text{PdCl}_2(\text{dppf})_2$ (0.21mmol), 120 mL of DMF and 8 mL of Et_3N were placed into the reaction flask and this mixture was stirred at 80°C for 2 h. The resulting mixture was poured into a CH_2Cl_2 /water two-phase system. The organic layer was collected, washed twice with 30 mL of 10% phosphoric acid, then with water and finally evaporated. The residue was passed through a column packed with SiO_2 using hexane/ CH_2Cl_2 = 1/1 as eluent. The resulting solution was evaporated, the residue washed with hexane and dried to give 0.6 g of diphenyl derivative. Yield 32%. The title compound was characterized by ^1H -NMR and ^{13}C -NMR spectroscopy.

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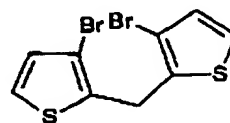
35

Synthesis of 2,5-diphenyl-7H-cycl penta[1,2-b:4,3-b']dithiophene (or 2,5-diphenyl - 7H-thieno[3',2':3,4]cyclopenta[b]thiophene)



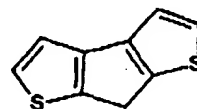
A 1.6 N *n*-BuLi solution (11.9 mL, 19 mmol) was added to a solution of 4.24 g of 3,3'-dibromo-5,5'-diphenyl-2,2'-dithienylmethane (8.65 mmol) in 50 mL of ether at -70°C . At the end of the addition, the reaction mixture was stirred for additional 30 min at the same temperature. Then 5.6 g of CuCl_2 (41.8 mmol) was added quickly. The resulting mixture was allowed to warm up to room temperature and stirred overnight. The final suspension was poured into water, the organic phase was separated and the solvent evaporated. The residue was passed through a column packed with SiO_2 , using hexane/ CH_2Cl_2 = 4/1 as eluent. The resulting solution was evaporated to leave a residue, which was washed with hexane and dried to give 1.1 g of crystalline solid. Yield 38%. The title compound was characterized by ^1H -NMR and ^{13}C -NMR spectroscopy.

Synthesis of 3,3'-dibromo-2,2'-dithienylmethane



49.59 g of 3,3',5,5'-tetrabromo-2,2'-dithienylmethane (0.1 mol), 19.6 g of zinc powder (0.3 mol), 120 mL of acetic acid and 40 mL of water were placed into the reaction flask. This suspension was refluxed under stirring for 3 h. The resulting mixture was poured into 300 mL of water and extracted twice with 200 mL of CH_2Cl_2 . The solvents were removed in vacuum and the residue was recrystallized from 100 mL of ethanol. Yield 27g (80%). The title compound was characterized by ^1H -NMR and ^{13}C -NMR spectroscopy.

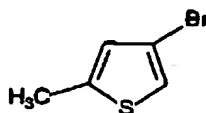
Synthesis of 7H-cyclopenta[1,2-b:4,3-b']dithiophene (or 7H-thieno[3',2':3,4]cyclopenta[b]thiophene)



(TC5420.EP)

A 1.6 N solution of *n*-BuLi (47ml, 75.2 mmol) was added to a solution of 11.5 g (34.0 mmol) of 3,3'-dibromo-2,2'-dithienylmethane in 200 mL ether at -70°C . After the addition was completed, the mixture was stirred for additional 30 min at the same temperature. Then 11.1g (82.6 mmol) of CuCl_2 was added quickly. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The resulting suspension was poured into water, the organic layer was collected and concentrated. The residue was passed through a column packed with SiO_2 using hexane or a mixture hexane/ether as eluent. The resulting solution was evaporated and the residue was recrystallized from pentane. Yield 1.2 g (20%). The title compound was characterized by ^1H -NMR and ^{13}C -NMR spectroscopy.

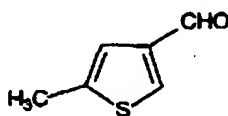
Synthesis of 2-methyl-4-bromo-thiophene



1 mol of 2-thiophenecarboxaldehyde was added to 2.5 mol of pulverized AlCl_3 under stirring keeping the temperature below 40°C . At the end of the addition the liquid complex was solidified; then 1.2 mol of bromine was carefully added dropwise under stirring. When the addition was complete, stirring became impossible because of the mixture solidified completely. This solid substance was poured into a mixture of ice (0.5 Kg) and hydrochloric acid (100 mL, 32%), then 300 mL of CH_2Cl_2 was added. The organic phase was separated and the solvent removed. The resulting substance (4-bromo-2-thiophenecarboxaldehyde) was dissolved in 700 mL of di(ethylene glycol) and the so-obtained solution was treated with 5.5 mol of hydrazine hydrate. The resulting mixture was refluxed for 30 min. After cooling up to room temperature, 2.75 mol of potassium hydroxide was added. After the gas evolution was over, the distillation was started and the fraction before 150°C was collected. This fraction represented the mixture of water and desired product: the organic layer was separated and distilled at $60^{\circ}\text{C}/10$ torr. Yield 52%.

^1H NMR (δ in ppm, CDCl_3): 6.99 (d, 1H, H_a); 6.69 (q, 1H, H_b); 2.48 (d, 3H, CH_3).

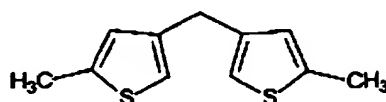
Synthesis of 2-methyl-4-formyl-thiophene



(TC5420.EP)

To a stirred solution of 44.26g of 2-methyl-4-bromo-thiophene (0.25 mol) in 300 mL of ether, 164 mL of a 1.6 M solution of *n*-BuLi (0.26 mol) was added at -70°C. The resulting solution was kept under stirring at -60 ÷ -70°C for 30 min and then was treated with 27.4 g of dimethylformamide (0.37 mol) in 100 mL of ether. The mixture was allowed to warm up to room temperature, then neutralized with 10% aqueous solution of NH₄Cl, washed with 10% aqueous solution of H₃PO₄ and finally with water up to neutral pH. The organic phase was collected, evaporated and distilled at 110°C/10mmHg. Yield 22.3 g (71%). The title compound was characterized by ¹H-NMR spectroscopy.

Synthesis of 2,2'-dimethyl-4,4'-dithienylmethane

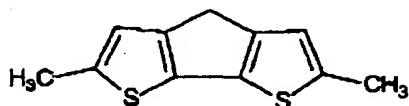


113 mL of 1.6 M *n*-BuLi solution (0.18 mol) was added to a solution of 31.3 g of 2-methyl-4-bromo-thiophene (0.177 mol) in 150 mL of ether at -70°C under stirring. The resulting solution was kept under stirring at -60 ÷ -70°C for 30 min and then was added of 22.3 g of 2-methyl-4-formyl-thiophene (0.177 mol) in 100 mL of ether. The mixture was allowed to warm up to room temperature, then neutralized with 10% aqueous solution of NH₄Cl and washed with water. The organic phase was separated and evaporated (crude bis(2-methyl-4-thienyl)methanol or 2,2'-dimethyl-4,4'-dithienyl carbinol).

A suspension of 35.5 g of AlCl₃ (0.266 mol) in 100 mL of ether was added slowly to a suspension of 10 g of LiAlH₄ (0.266 mol) in 100 mL of ether. The resulting mixture was treated with the solution of the carbinol obtained as above described in 100 mL ether. Then the reaction mixture was refluxed for additional 1 h, cooled up to room temperature and finally added of 100 mL of ethyl acetate. After it was treated with 300 mL of water and 300 mL of ether. The organic phase was collected, washed with water, dried by MgSO₄ and evaporated. The residue was distilled at 90÷110°C/0.5 mmHg. Yield 23.2g (63%).

The title compound was characterized by ¹H-NMR spectroscopy.

Synthesis of 2,6-dimethyl-4H-cycl penta[2,1-b:3,4-b']dithiophene (or 2,6-dimethyl-4H-thieno[3',2':2,3]cyclopenta[b]thiophene)



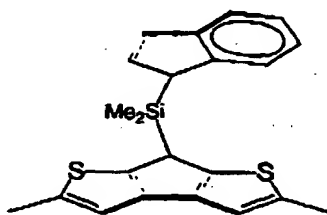
1.04 g of 2,2'-dimethyl-4,4'-dithienylmethane (5 mmol) was dissolved in 30 mL of ether and added of 9 mL of 1.6 M solution of *n*-BuLi (14.4 mmol) and of 1.74 g of TMEDA (15 mmol) at -70°C under stirring. The resulting mixture was allowed to warm up to room temperature, stirred for 1 h, then cooled again to -70°C and treated with 2.7 g of CuCl₂ (20 mmol). The resulting reaction mixture was allowed to warm up to room temperature and added of 30 mL of water. The organic phase was collected and passed through a column packed with silica gel. The resulting solution was evaporated to give 0.34 g of the product. Yield 34%.

The title compound was characterized by ¹H-NMR spectroscopy.

PREPARATION OF THE LIGANDS

Example 1

Synthesis of 1-(indenyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene) dimethylsilane



3.13 mL of a 1.6 M solution of *n*-BuLi (5 mmol) was added at -70°C to a solution of 1.03 g (5 mmol) of 2,5-dimethyl-7H-cyclopenta[1,2-b:4,3-b']-dithiophene in 20 mL of ether. The resulting mixture was stirred for additional 30 min at 0°C, then cooled again to -70°C and treated with 1.04 g (5 mmol) of chloro(1-indenyl) dimethylsilane in 10 mL of ether. The reaction mixture was allowed to warm up to room temperature and then treated with a saturated aqueous solution of NH₄Cl. The organic phase was isolated and the solvent was removed to give the crude product as an orange oil in 100% yield (1.89 g).

The title compound was characterized by ¹H-NMR spectroscopy.

(TC:5420.EP)

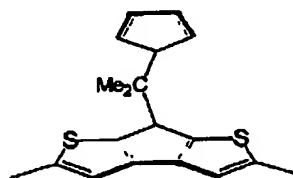
Example 2

Synthesis of (2-methyl-1-indenyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene) dimethylsilane.

The procedure for the synthesis of 1-(indenyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene) dimethylsilane described in Example 1 was followed, except that chloro(2-methyl-1-indenyl) dimethylsilane was used instead of the chloro(1-indenyl) dimethylsilane.

Example 3

Synthesis of 2,2-(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene)propane



3.13 mL of a 1.6 M solution of *n*-BuLi (5 mmol) was added at -70°C to a solution of 1.03 g (5 mmol) of 2,5-dimethyl-7H-cyclopenta[1,2-b:4,3-b']-dithiophene in 20 mL of ether. The resulting mixture was stirred for additional 30 min at 0°C , then cooled again to -70°C and treated with 0.6 g (5 mmol) of 3,6,6-trimethylfulvene in 10 mL of ether. The reaction mixture was allowed to warm up to room temperature and then treated with a saturated aqueous solution of NH_4Cl . The organic phase was isolated, dried by MgSO_4 and concentrated. The residue was recrystallized from hexane. Yield 1.0 g (62%). The title compound was characterized by $^1\text{H-NMR}$ spectroscopy.

Example 4

Synthesis of 2,2-(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene)propane

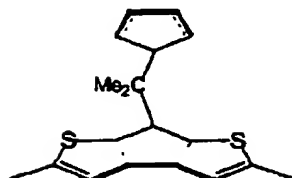
The same procedure as described in Example 3 was followed (see below for details).

Example 5

Synthesis of 2,2-(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-

(TC5420.EP)

40

b']-dithiophene)propane

3.13 mL of a 1.6 M solution of *n*-BuLi (5 mmol) was added at -70°C to a solution of 1.03 g (5 mmol) of 2,5-dimethyl-7H-cyclopenta[1,2-b:4,3-b']-dithiophene in 20 mL of ether. The resulting mixture was stirred for additional 30 min at 0°C , then cooled again to -70°C and treated with 0.74 g (5 mmol) of 3-isopropyl-6,6-dimethylfulvene in 10 mL of ether. The reaction mixture was allowed to warm up to room temperature and then treated with a saturated aqueous solution of NH_4Cl . The organic phase was isolated, dried by MgSO_4 , and concentrated. The residue was recrystallized from hexane. Yield 0.85 g (48%).

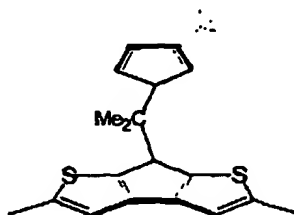
The title compound was characterized by ^1H -NMR spectroscopy.

Example 6**Synthesis of 2,2-(3-isopropyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopenta [1,2-b:4,3-b']-dithiophene)propane**

The same procedure as described in Example 5 was followed (see below for details).

Example 7**Synthesis of 2,2-(3-isopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopenta[2,1-b:3,4-b']dithiophene)propane**

The same procedure as described in Example 5 was followed (see below for details).

Example 8**Synthesis of 2,2-(3-tert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene)propane**

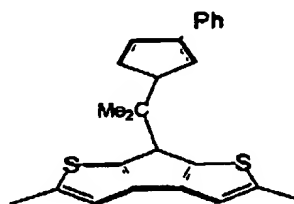
3.13 mL of a 1.6 M solution of *n*-BuLi (5 mmol) was added at -70°C to a solution of 1.03 g

(TC5420.EP)

(5 mmol) of 2,5-dimethyl-7H-cyclopenta[1,2-b:4,3-b']-dithiophene in 20 mL of ether. The resulting mixture was stirred for additional 30 min at 0°C, then cooled again to -70°C and treated with 0.81 g (5 mmol) of 3-tert-butyl-6,6-dimethylfulvene in 10 mL of ether. The reaction mixture was allowed to warm up to room temperature and then treated with a saturated aqueous solution of NH₄Cl. The organic phase was isolated, dried by MgSO₄ and concentrated. The residue was recrystallized from hexane. Yield 0.94 g (51%). The title compound was characterized by ¹H-NMR spectroscopy.

Example 9

Synthesis of 2,2-(3-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene)propane



3.13 mL of a 1.6 M solution of *n*-BuLi (5 mmol) was added at -70°C to a solution of 1.03 g (5 mmol) of 2,5-dimethyl-7H-cyclopenta[1,2-b:4,3-b']-dithiophene in 20 mL of ether. The resulting mixture was stirred for additional 30 min at 0°C, then cooled again to -70°C and treated with 0.98 g (5 mmol) of 3-phenyl-6,6-dimethylfulvene in 10 mL of ether. The reaction mixture was allowed to warm up to room temperature and then treated with a saturated aqueous solution of NH₄Cl. The organic phase was isolated, dried by MgSO₄ and concentrated. The residue was recrystallized from hexane. Yield 0.57 g (29%).

The title compound was characterized by ¹H-NMR spectroscopy.

Example 10

Synthesis of 2,2-(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene) propane

The same procedure as described in Example 9 was followed (see below for details).

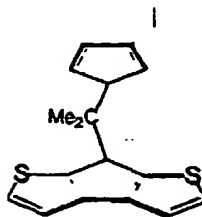
Example 11

Synthesis of 2,2-(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-

(IC5420.EP)

42

dithiophene)pr pane



3.13 mL of 1.6 M solution of *n*-BuLi (5 mmol) was added to a solution of 0.89 g (5 mmol) of the 7H-cyclopenta[1,2-b:4,3-b']dithiophene in 20 mL of THF at -70°C . The resulting mixture was stirred for additional 30 min at 0°C , then cooled again to -70°C and treated with 0.74 g (5 mmol) of 3-isopropyl-6,6-dimethylfulvene in 10 mL of ether. The reaction mixture was allowed to warm up to room temperature and then treated with a saturated aqueous solution of NH_4Cl . The organic phase was isolated, dried by MgSO_4 and concentrated. The residue was passed through a column packed with silica gel using hexane as eluent ($R_f = 0.8$). Yield 1.05 g (64%). The title compound was characterized by $^1\text{H-NMR}$ spectroscopy.

PREPARATION OF THE METALLOCENES

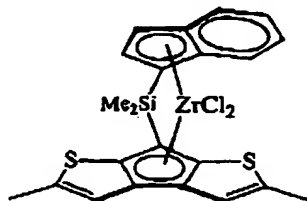
Example 12 (comparison)

Synthesis of isopropylidene{(cyclopentadienyl)-7-(cyclopenta[1,2-b:4,3-b']-dithiophene)}zirconium dichloride $[\text{Me}_2\text{C}(\text{Cp})(7\text{-Th}_2\text{-Cp})\text{ZrCl}_2]$

It was carried out as described in the Example 6 of WO 98/22486.

Example 13

Synthesis of dimethylsilyl{(1-indenyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene)} zirconium dichloride $[\text{Me}_2\text{Si}(\text{Ind})(7\text{-MeTh}_2\text{-Cp})\text{ZrCl}_2]$



6.25 mL of a 1.6 M *n*-BuLi (10.0 mmol) solution was added at -70°C to a solution of 1.89 g (5.0 mmol) of 1-(indenyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)dimethylsilane in 20 mL of ether. The mixture was allowed to warm up to 0°C

(TC5420.EP)

and then was treated with 1.16 g (5.0 mmol) of $ZrCl_4$. The reaction mixture was refluxed under stirring for 3 h and then added of 50 mL of CH_2Cl_2 at room temperature. The resulting solution was isolated and evaporated. The residue was recrystallized from CH_2Cl_2 /hexane. Yield 0.81 g (30%). The title compound was characterized by 1H -NMR spectroscopy.

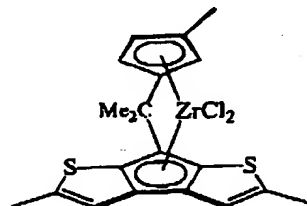
Example 14

Synthesis of dimethylsilyl{(2-methyl-1-indenyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene)} zirconium dichloride [$Me_2Si(2-Me-Ind)(7-MeTh,-Cp)ZrCl_2$]

The procedure described in Example 13 was followed, except that (2-methyl-1-indenyl)-7-(2,5-dimethyl-cyclopenta [1,2-b:4,3-b']-dithiophene)dimethylsilane was used instead of the 1-(indenyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)dimethylsilane.

Example 15

Synthesis of isopropylidene{ (3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene) } zirconium dichloride [$Me_2C(3-Me-Cp)(7-MeTh,-Cp)ZrCl_2$]

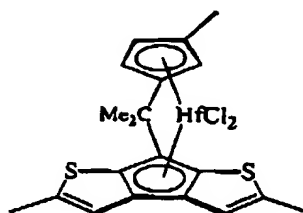
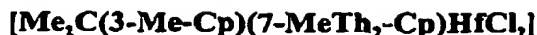


2.3 mL of 1.6 M *n*-BuLi solution (3.7 mmol) was added at $-70^\circ C$ to a suspension of 0.6 g (1.85 mmol) of 2,2-(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm up to $0^\circ C$ and then was treated with 0.43 g (1.85 mmol) of $ZrCl_4$. The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH_2Cl_2 . Yield 0.72 g (80%). The title compound was characterized by 1H -NMR spectroscopy.

Example 16

Synthesis of isopropylidene{ (3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene) } hafnium dichloride

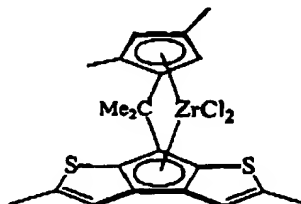
(TC.5420.EP)



2.5 mL of 1.6 M *n*-BuLi solution (4.0 mmol) was added at -70°C to a suspension of 0.65 g (2.0 mmol) of 2,2-(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm up to 0°C and then was treated with 0.64 g (2.0 mmol) of HfCl_4 . The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH_2Cl_2 . Yield 0.48 g (42%). The title compound was characterized by $^1\text{H-NMR}$ spectroscopy.

Example 17

Synthesis of isopropylidene{ (2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene) }zirconium dichloride



3.13 mL of 1.6 M *n*-BuLi solution (5.0 mmol) was added at -70°C to a solution of 1.03 g (5.0 mmol) of 2,5-dimethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene in 20 mL of ether. The resulting mixture was stirred for additional 30 min at 0°C , then cooled again to -70°C and treated with 0.67 g (5.0 mmol) of 1,3,6,6-tetramethylfulvene in 10 mL of ether. The reaction mixture was allowed to warm up to room temperature and stirred for 8 h. Successively, it was cooled to -30°C to add 3.13 mL of 1.6 M *n*-BuLi solution (5.0 mmol). The mixture was then allowed to warm up to 0°C and treated with 1.16 g (5.0 mmol) of ZrCl_4 . The reaction mixture was refluxed under stirring for 3 h and 10 mL of CH_2Cl_2 was added at room temperature. The solution was isolated, concentrated and the residue was

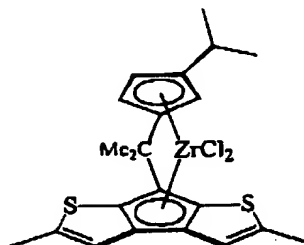
(TC5420.FP)

45

recrystallized from CH_2Cl_2 /hexane. Yield 0.58 g (23% towards 2,5-dimethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene).

Example 18

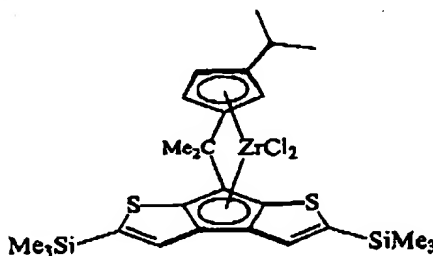
Synthesis of isopropylidene{ (3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene) }zirconium dichloride
[$\text{Me}_2\text{C}(3\text{-iPr-Cp})(7\text{-MeTh}_2\text{-Cp})\text{ZrCl}_2$]



3.75 mL of 1.6 M *n*-BuLi solution (6.0 mmol) was added at -70°C to a suspension of 1.06 g (3.0 mmol) of 2,2-(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm up to 0°C and then was treated with 0.7 g (3.0 mmol) of ZrCl_4 . The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH_2Cl_2 . Yield 1.24 g (80%). The title compound was characterized by $^1\text{H-NMR}$ spectroscopy.

Example 19

Synthesis of isopropylidene{ (3-isopropyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopenta[1,2-b:4,3-b']-dithiophene) }zirconium dichloride
[$\text{Me}_2\text{C}(3\text{-iPr-Cp})(7\text{-TMSTh}_2\text{-Cp})\text{ZrCl}_2$]



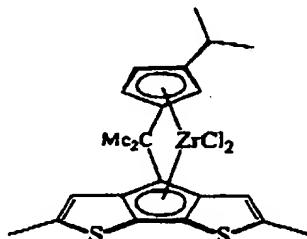
3.05 mL of 1.6 M *n*-BuLi solution (4.9 mmol) was added at -70°C to a solution of 1.57 g (4.86 mmol) of 2,5-ditrimethylsilyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene in 20 mL

(1C5420.EP)

ether. The resulting mixture was stirred for additional 30 min at 0°C, then cooled again to -70°C and treated with 0.72 g (4.9 mmol) of 3-isopropyl-6,6-dimethylfulvene in 10 mL of ether. The reaction mixture was allowed to warm up to room temperature and stirred for 4 h. Successively, it was cooled to -30°C to add 3.05 mL of 1.6 M *n*-BuLi solution (4.9 mmol). The mixture was allowed to warm up to 0°C and treated with 1.14 g (4.9 mmol) of ZrCl₄. The resulting reaction mixture was refluxed under stirring for 3 h, then the solution was isolated and concentrated. The residue was recrystallized from pentane. Yield 0.23 g (7.4% towards 2,5-ditrimethylsilyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene). The title compound was characterized by ¹H-NMR spectroscopy.

Example 20

Synthesis of isopropylidene{ (3-isopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopenta[2,1-b:3,4-b']-dithiophene) }zirconium dichloride
 $[\text{Me}_2\text{C}(\text{3-iPr-Cp})(\text{4-MeTh}_2\text{-Cp})\text{ZrCl}_2]$

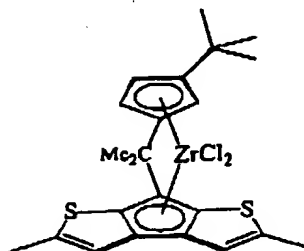


3.13 mL of 1.6 M *n*-BuLi solution (5.0 mmol) was added at -70 °C to a solution of 1.03 g (5.0 mmol) of 2,6-dimethyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene in 20 mL of ether. The resulting mixture was stirred for additional 30 min at 0°C, then cooled again to -70°C and treated with 0.74 g (5.0 mmol) of 3-isopropyl-6,6-dimethylfulvene in 10 mL of ether. The mixture was allowed to warm up to room temperature and stirred for 4 h. Successively, it was cooled to -30°C to add 3.13 mL of 1.6 M *n*-BuLi solution (5.0 mmol). The reaction mixture was allowed to warm up to 0°C and treated with 1.16 g (5.0 mmol) of ZrCl₄. The resulting reaction mixture was refluxed under stirring for 3 h and 30 mL of CH₂Cl₂ was added at room temperature. The solution was isolated and concentrated. The residue was recrystallized from CH₂Cl₂/hexane. Yield 0.87g (34% towards 2,6-dimethyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene). The title compound was characterized by ¹H-NMR spectroscopy.

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Example 21 (c mparis n)

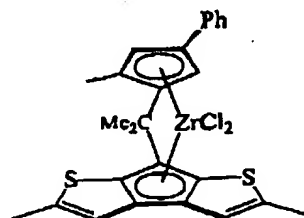
Synthesis of isopropylidene{ (3-tert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene) }zirconium dichloride
 $[\text{Me}_2\text{C}(3\text{-tBu-Cp})(7\text{-MeTh}_2\text{-Cp})\text{ZrCl}_2]$



3.75 mL of 1.6 M *n*-BuLi solution (6.0 mmol) was added at -70°C to a suspension of 1.11 g (3.0 mmol) of 2,2-(3-tert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm up to 0°C and treated with 0.7 g (3.0 mmol) of ZrCl_4 . The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH_2Cl_2 . Yield 1.27 g (80%). The title compound was characterized by $^1\text{H-NMR}$ spectroscopy.

Example 22

Synthesis of isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta-[1,2-b:4,3-b']-dithiophene)zirconium dichloride
 $[\text{Me}_2\text{C}(2\text{-Me-4-Ph-Cp})(7\text{-MeTh}_2\text{-Cp})\text{ZrCl}_2]$



3.75 mL (6.0 mmol) of 1.6 M *n*-BuLi solution was added at -70°C to a suspension of 1.21 g (3.0 mmol) of 2,2-(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm up to 0°C and treated with 0.7 g (3.0 mmol) of ZrCl_4 . The reaction mixture was refluxed under stirring for 3 h, then the yellowish-brown precipitate was filtered, washed twice with ether,

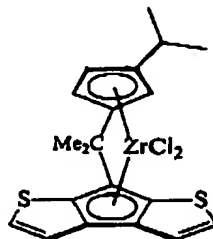
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dried and finally recrystallized from CH_2Cl_2 /hexane. Yield 0.93 g (55%).

The desired title compound was characterized by ^1H -NMR spectroscopy.

Example 23

Synthesis of isopropylidene(3-isopropyl-cyclopentadienyl)-7-(cyclopenta[1,2-b:4,3-b']-dithiophene) zirconium dichloride $[\text{Me}_2\text{C}(3\text{-iPr-Cp})(7\text{-Th}_2\text{-Cp})\text{ZrCl}_2]$



A solution of 1.05 g (3.22 mmol) of 2,2-(3-isopropyl-cyclopentadienyl)-7-(cyclopenta [1,2-b:4,3-b']-dithiophene)propane in a mixture of 10 mL of ether and 60 mL of hexane was treated with 4.1 mL (6.6 mmol) of a 1.6 M *n*-BuLi solution at -70°C . The mixture was allowed to warm up to 0°C and treated with 0.75 g (3.2 mmol) of ZrCl_4 . The resulting reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with hexane, dried and finally recrystallized from CH_2Cl_2 /hexane. Yield 0.32 g (21%). The title compound was characterized by ^1H -NMR spectroscopy.

PROPYLENE POLYMERIZATION

Polymerization Examples 1-16 and Comparative Examples 17-18

MAO was a commercial product (Witco, 10 % w/w in toluene, 1.7 M in Al) which was used as received. The catalyst mixture was prepared by dissolving the desired amount of the metallocene with the proper amount of the MAO solution, obtaining a solution which was stirred for 10 min at ambient temperature before being injected into the autoclave. 1 mmol of $\text{Al}(i\text{-Bu})_3$ (as a 1M solution in hexane) and 290 g of propylene were charged at room temperature in a 1-L jacketed stainless-steel autoclave, equipped with magnetically driven stirrer and a 35-mL stainless-steel vial, connected to a thermostat for temperature control, previously purified by washing with an $\text{Al}(i\text{-Bu})_3$ solution in hexanes and dried at 50°C in a stream of propene. The autoclave was then thermostatted at 2°C below the polymerization temperature, and then the toluene solution containing the catalyst/cocatalyst mixture was injected in the autoclave by means of nitrogen pressure through the stainless-steel vial, the

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temperature rapidly raised to the polymerization temperature and the polymerization carried out at constant temperature for 1 hour. After venting the unreacted monomer and cooling the reactor to room temperature, the polymer was dried under reduced pressure at 60 °C.

The polymerization conditions are reported in Table 1.

The characterization data of the obtained polymers are shown in Table 2.

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Table 1

Example	metallocene		Al/Zr molar	Time (h)	Tp (°C)	yield (g)	Activity (Kg/g _{cat} .h)
	type	mg					
1	Me ₂ C(3-MeCp)(7-MeTh ₂ -Cp)ZrCl ₂	0.8	3000	0.75	60	123	154
2	Me ₂ C(3-iPrCp)(7-MeTh ₂ -Cp)ZrCl ₂	0.3	500	1	60	87	291
3	Me ₂ C(3-iPrCp)(7-MeTh ₂ -Cp)ZrCl ₂	0.3	1000	1	60	111	370
4	Me ₂ C(3-MeCp)(7-MeTh ₂ -Cp)HfCl ₂	2	1000	1	60	23	117
5	Me ₂ C(3-iPropCp)(7-TMSTh ₂ -Cp)ZrCl ₂	1	500	1	60	81	81
6	Me ₂ C(3-iPropCp)(4-MeTh ₂ -Cp)ZrCl ₂	1	500	1	60	31	31
7	Me ₂ Si(Ind)(7-MeTh ₂ -Cp)ZrCl ₂	1	500	1	60	36	36
8	Me ₂ C(2-Me-4-Ph-Cp)(7-MeTh ₂ -Cp)ZrCl ₂	1	500	1	60	240	240
9	Me ₂ C(2,4-Me ₂ -Cp)(7-MeTh ₂ -Cp)ZrCl ₂	1	500	1	60	94	94
10	Me ₂ Si(2-Me-Ind)(7-MeTh ₂ -Cp)ZrCl ₂	1	500	1	60	79	79
11	Me ₂ C(3-iPr-Cp)(7-Th ₂ -Cp)ZrCl ₂	1	500	1	60	44	44
12	Me ₂ C(2-Me-4-iPr-Cp)(7-MeTh ₂ -Cp)ZrCl ₂	1	500	1	60	120	120
13	Me ₂ Si(3-TMS-Cp)(7-MeTh ₂ -Cp)ZrCl ₂	1	500	1	60	300	300
14	Me ₂ C(2-Me-4-PhCp)(7-MeTh ₂ -Cp)ZrCl ₂	1	500	1	60	13	13
15	Me ₂ C(2,4-Me ₂ -Cp)(7-TMSTh ₂ -Cp)ZrCl ₂	1	500	1	60	119	119
16	Me ₂ Si(2,4-Me ₂ -Cp)(7-MeTh ₂ -Cp)ZrCl ₂	1	500	1	60	64	64
17 (comp)	Me ₂ C(Cp)(7-Th ₂ -Cp)ZrCl ₂	1	4500	1	50	29	29
18 (comp)	Me ₂ C(3-tBu-Cp)(7-MeTh ₂ -Cp)ZrCl ₂	1	3000	1	60	61	122

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Table 2

Ex.	Metallocene	Exp. Triad			I.V dl/g	ΔH	Tm (°C)
		Distribution %					
		Mm	rm	rr			
1	Me ₂ C(3-MeCp)(7-MeTh ₂ -Cp)ZrCl ₂	58.7	23.0	18.3	0.54	13	80
2	Me ₂ C(3-iPrCp)(7-MeTh ₂ -Cp)ZrCl ₂	73.1	16.9	9.9	0.83	40	103
3	Me ₂ C(3-iPrCp)(7-MeTh ₂ -Cp)ZrCl ₂	-	-	-	0.73	39	100
4	Me ₂ C(3-MeCp)(7-MeTh ₂ -Cp)HfCl ₂	55.5	29.6	14.8	0.77	n.d.	n.d.
5	Me ₂ C(3-iPropCp)(7-TMSTh ₂ -Cp)ZrCl ₂	76.0	16.0	8.0	0.92	47	107
6	Me ₂ C(3-iPropCp)(4-MeTh ₂ -Cp)ZrCl ₂	50.8	24.3	25.1	0.64	n.d.	n.d.
7	Me ₂ Si(Ind)(7-MeTh ₂ -Cp)ZrCl ₂	79.9	13.6	6.5	1.25	61	114
8	Me ₂ C(2-Me-4-Ph-Cp)(7-MeTh ₂ -Cp)ZrCl ₂	42.6	29.2	28.2	0.90	Amorphous	
9	Me ₂ C(2,4-Me ₂ -Cp)(7-MeTh ₂ -Cp)ZrCl ₂	n.d.	n.d.	n.d.	0.79	Amorphous	
10	Me ₂ Si(2-Me-Ind)(7-MeTh ₂ -Cp)ZrCl ₂	81.3	12.2	6.5	2.34	47	101
11	Me ₂ C(3-iPr-Cp)(7-Th ₂ -Cp)ZrCl ₂	54.0	26.9	19.1	0.74	Amorphous	
12	Me ₂ C(2-Me-4-iPr-Cp)(7-MeTh ₂ -Cp)ZrCl ₂	66.5	20.5	13.0	1.06	21	81
13	Me ₂ Si(3-TMS-Cp)(7-MeTh ₂ -Cp)ZrCl ₂	n.d.	n.d.	n.d.	0.72	Amorphous	
14	Me ₂ C(2-Me-4-PhCp)(7-MeTh ₂ -Cp)ZrCl ₂	n.d.	n.d.	n.d.	0.64	Amorphous	
15	Me ₂ C(2,4-Me ₂ -Cp)(7-TMSTh ₂ -Cp)ZrCl ₂	n.d.	n.d.	n.d.	0.8	Amorphous	
16	Me ₂ Si(2,4-Me ₂ -Cp)(7-MeTh ₂ -Cp)ZrCl ₂	84.0	10.6	5.4	1.24	64	123
17 (comp)	Me ₂ C(Cp)(7-Th ₂ -Cp)ZrCl ₂	2.8	12.1	85.2	0.98	27	110
18 (comp)	Me ₂ C(3-tBu-Cp)(7-MeTh ₂ -Cp)ZrCl ₂	89.2	7.2	3.5	0.58	91	139

n.d.: not determined

CLAIMS

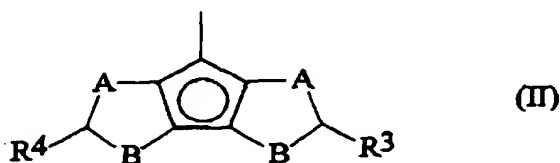
1. A metallocene compound of the general formula (I):



wherein

L is a divalent group bridging the moieties G and Z, selected from CR^1R^2 , SiR^1R^2 and $(\text{CR}^1\text{R}^2)_2$, R^1 and R^2 , same or different from each other, are selected from hydrogen, a $\text{C}_1\text{-C}_{20}$ -alkyl, $\text{C}_3\text{-C}_{20}$ -cycloalkyl, $\text{C}_2\text{-C}_{20}$ -alkenyl, $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_7\text{-C}_{20}$ -alkylaryl, $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing a heteroatom, which can form a ring having 3 to 8 atoms which can bear a substituent;

Z is a moiety of formula (II):

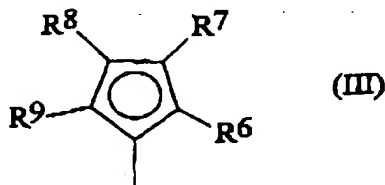


wherein

R^3 and R^4 , same or different from each other, are selected from hydrogen, a $\text{C}_1\text{-C}_{20}$ -alkyl, $\text{C}_3\text{-C}_{20}$ -cycloalkyl, $\text{C}_2\text{-C}_{20}$ -alkenyl, $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_7\text{-C}_{20}$ -alkylaryl, $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing a heteroatom, at least one of R^3 and R^4 being different from hydrogen;

A and B are selected from S, O or CR^5 , wherein R^5 is selected from hydrogen, a $\text{C}_1\text{-C}_{20}$ -alkyl, $\text{C}_3\text{-C}_{20}$ -cycloalkyl, $\text{C}_2\text{-C}_{20}$ -alkenyl, $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_7\text{-C}_{20}$ -alkylaryl, $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing a heteroatom, either A or B being different from CR^5 , and wherein the rings containing A and B have a double bond in the allowed position;

G is a moiety of formula (III):



wherein

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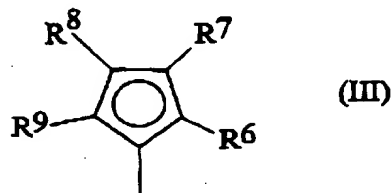
R^6 , R^7 , R^8 and R^9 , same or different from each other, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom, and R^6 and R^7 and/or R^8 and R^9 can form a ring comprising from 3 to 8 atoms, which can bear substituents, with the provisions that R^7 is different from R^8 and when R^7 is a tert-butyl radical, R^8 is not hydrogen;

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements (new IUPAC version),

X, same or different, is selected from a halogen atom, a R^{10} , OR^{10} , OSO_2CF_3 , $OCOR^{10}$, SR^{10} , NR^{10}_2 or PR^{10}_2 group, wherein the substituents R^{10} are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms;

p is an integer of from 0 to 3, being equal to the oxidation state of the metal M minus 2.

2. The metallocene according to claim 1, wherein the transition metal M is selected from titanium, zirconium and hafnium.
3. The metallocene according to any of claims 1 and 2, wherein the X substituents are chlorine atoms or methyl groups
4. The metallocene according to any of claims 1 to 3, wherein L is $=CMe_2$ or $=SiMe_2$.
5. The metallocene according to any of claims 1 and 4, wherein one of A and B is a sulfur atom and the other is a CH group.
6. The metallocene according to claim 5, wherein R^3 and R^4 are the same and are selected from a C_1 - C_{20} -alkyl group, which can contain a silicon atom.
7. The metallocene according to claim 1, wherein G is a moiety of formula (III):



wherein

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R^6 and R^9 , same or different from each other, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom,

R^7 is selected from a C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or a $QR^{11}R^{12}R^{13}$ group, wherein Q is selected from C, Si, Ge;

R^{11} , R^{12} and R^{13} , same or different from each other, are hydrogen, C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radicals, optionally containing a heteroatom, with the proviso that when Q is a carbon atom, at least one of R^{11} , R^{12} and R^{13} is a hydrogen atom, and

R^8 is hydrogen.

8. The metallocene according to claim 7, wherein R^7 is selected from phenyl, a $CHR^{11}R^{12}$ and a $SiR^{11}R^{12}R^{13}$ group, wherein R^{11} , R^{12} and R^{13} are hydrogen or C_1 - C_{20} -alkyl groups.
9. The metallocene according to claim 8, wherein $QR^{11}R^{12}R^{13}$ is an isopropyl or a trimethylsilyl group.
10. The metallocene according to any of claims 7 to 9, wherein the metallocene is isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
dimethylsilandiyl(3-trimethylsilyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
isopropylidene(2-methyl-4-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
isopropylidene(3-isopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride;
isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(3-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

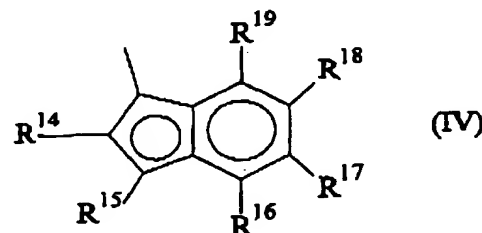
isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

dimethylsilandiyl(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride; and

isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)hafnium dichloride

11. The metallocene according to claim 1, wherein G is a moiety of formula (IV):



wherein

R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸ and R¹⁹, same or different, are selected from hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms, any of two adjacent R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸ and R¹⁹ can form a ring comprising 4 to 8 atoms which can bear substituents, and the benzene ring can be perhydrated.

12. The metallocene according to claim 11, wherein R¹⁵, R¹⁶, R¹⁷, R¹⁸ and R¹⁹ are hydrogen and R¹⁴ is a C₁-C₂₀-alkyl group.

13. The metallocene according to any of claims 11 to 12, wherein the metallocene is dimethylsilandiyl-1-(indenyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

dimethylsilandiyl-1-(2-methyl-indenyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-

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dithiophene)zirconium dichloride;

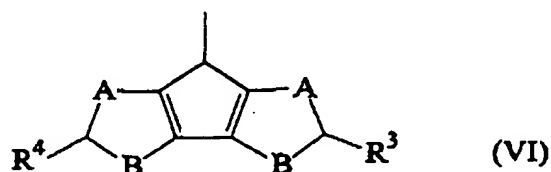
dimethylsilandiyl-1-(indenyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride.

14. A ligand of formula (V):

LG'Z' (V)

wherein L is defined as in claim 1:

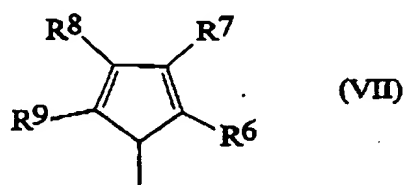
Z' is a moiety of formula (VI):



and its double bond isomers;

wherein A, B, R³ and R⁴ are defined as in claim 1;

G' is a moiety of formula (VII):



and its double bond isomers;

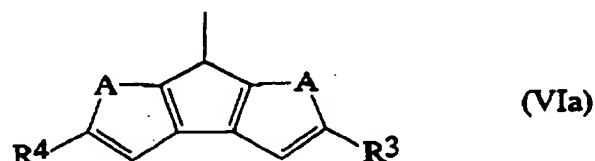
wherein R⁶, R⁷, R⁸ and R⁹ have the meaning as defined in any of claims 1 to 13.

15. A process for the preparation of a ligand of formula (V):

LG'Z' (V)

wherein G' and L are defined as in claim 14;

Z' is a moiety of formula (VIa):



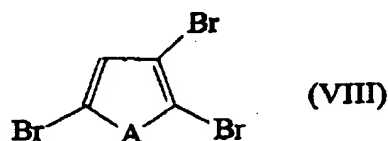
and its double bond isomers;

wherein A is sulfur or oxygen, R³ and R⁴ are the same and are selected from a

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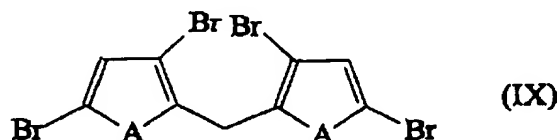
C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom; comprising the following steps:

- a) contacting a compound of formula (VIII):



with a base selected from an organic lithium compound, sodium or potassium; and subsequent treatment with a formic ester, wherein the molar ratio between said ester and the compound of formula (VIII) is at least 1:2, and subsequently

- b) treating with a reducing agent in order to obtain a compound of formula (IX):



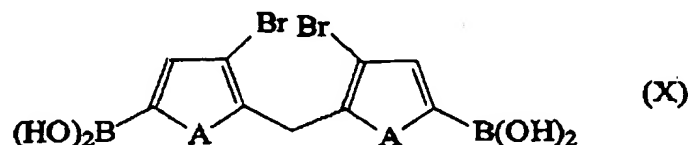
- c) contacting with a base selected from an organic lithium compound, sodium or potassium;

and subsequent treatment with an alkylating agent,

- d) contacting with a base selected from an organic lithium compound, sodium or potassium;

and subsequent treatment with a coupling agent; or contacting the above defined compound of formula (VIII) with a base selected from an organic lithium compound, sodium or potassium;

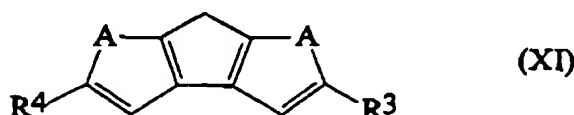
followed by treating with an ester of boric acid and a protonating agent in order to obtain the compound of formula (X):



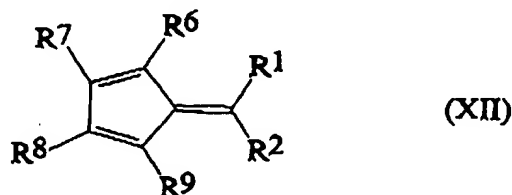
and subsequently contacting with a mixture of an alkylating agent in the presence of a transition metal complex compound followed by above step

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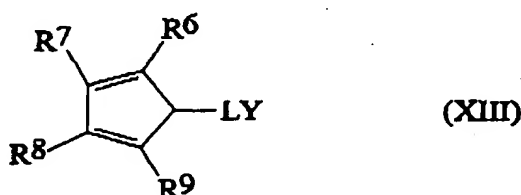
d), in order to obtain the compound of formula (XI);



- f) contacting the compound of the formula (XI) with a base selected from the group consisting of metallic sodium and potassium, sodium and potassium hydroxide and an organic lithium compound, wherein the molar ratio between the compound of the formula (XI) and said base is at least 1;
- f') when L is $\text{CR}^{11}\text{R}^{12}$ contacting the corresponding anionic moiety of the formula (XI) with a compound of the general formula (XII):



wherein R^1 , R^2 , R^6 , R^7 , R^8 and R^9 have the meaning as defined in claim 1;
or, when L is a SiR^1R^2 or $(\text{CR}^1\text{R}^2)_2$, contacting the corresponding anionic compounds of the formula (XI) with a compound of general formula (XIII):



wherein R^6 , R^7 , R^8 and R^9 are defined as above and Y is a halogen radical selected from the group consisting of fluoride, chloride, bromide and iodide;

- g) treating with a protonating agent.
- 16 The process according to claim 15, wherein the reducing agent is a mixture of $\text{AlCl}_3/\text{LiAlH}_4$ or a mixture of triethylsilane (Et_3SiH) and CF_3COOH .
 17. The process according to claim 15, wherein the base is butyllithium.
 18. The process according to claim 15, wherein the organic acid ester is an ester of formic acid.

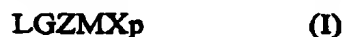
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19. The process according to claim 15, wherein the alkylation agent is selected from dimethylsulphate (Me_2SO_4), trimethylchlorosilane (Me_3SiCl) and a mixture of compounds of formulae $\text{R}^3\text{Y}'$ and $\text{R}^4\text{Y}'$, wherein R^3 and R^4 are defined as in claim 1 and Y' is selected from chloride, bromide and iodide.
20. The process according to claim 15, wherein the coupling agent is selected from the group consisting of copper chloride, iodide and Mg/Pd .
21. The process according to claim 15, wherein the transition metal complex compound is $\text{PdCl}_2(\text{dppf})$.
22. The process according to claim 15, wherein Y is a chloride radical.
23. The process according to claim 15, wherein the base used for the preparation of the corresponding anionic form of the compound of formula (VIII) is butyllithium.
24. The process according to claim 15, wherein the compound of formula (XII) is selected from 3,6,6-trimethylfulvene and 3-isopropyl-6,6-dimethylfulvene.
25. A process for the preparation of a metallocene compound as defined in any of claims 1 to 13, obtainable by contacting the ligand of general formula (V) with a compound capable of forming the corresponding dianionic compound thereof and thereafter with a compound of general formula MX_{p+2} , wherein M , X and p are defined as in claim 1.
26. The process according to claim 25, wherein the compound able to form said corresponding dianionic compound is selected from the group consisting of hydroxides of alkali- and earth-alkali metals, metallic sodium and potassium, and organometallic lithium salts.
27. The process according to claim 26, wherein the compound able to form said corresponding dianionic compound is butyllithium.
28. The process according to claim 27, wherein the compound of formula MX_{p+2} is selected from titanium-, zirconium- and hafniumtetrachloride.
29. A catalyst obtainable by contacting:
 - (A) a metallocene compound of formula (I) according to any of claims 1 to 13, and
 - (B) an alumoxane and/or a compound capable of forming an alkyl metallocene.
30. The catalyst according to claim 29, wherein said alumoxane is obtained by contacting

water with an organo-aluminium compound of formula AlR^{20} , or $Al_2R^{20}_6$, wherein the R^{20} substituents are defined as R^1 .

31. The catalyst according to claim 30, wherein the molar ratio between the aluminium and water is in the range of 1:1 and 100:1.
32. The catalyst according to claim 29, wherein said alumoxane is methylalumoxane (MAO), isobutylalumoxane (TIBAO) and 2,4,4-trimethyl-pentylalumoxane (TIOAO).
33. The catalyst according to claim 29, wherein the compound capable of forming a metallocene alkyl cation is a compound of formula D^+E^- , wherein D^+ is a Brønsted acid, able to give a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and E^- is a compatible anion, which does not coordinate, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently liable to be able to be removed from an olefinic substrate.
34. The catalyst according to claim 33, wherein the anion E^- comprises one or more boron atoms.
35. The catalyst according to claim 29, wherein the molar ratio between the aluminium and the metal of the metallocene compound is comprised between 10:1 and 20000:1.
36. A process for the preparation of polymers of alpha-olefins in the presence of a catalyst comprising the product obtainable by contacting:

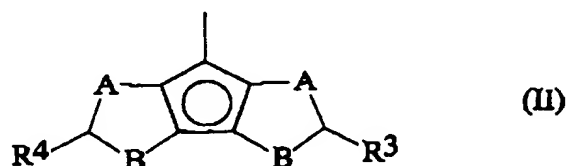
(A) a metallocene compound of the general formula (I):



wherein

L, M, X and p are defined as in any of claims 1 to 13;

Z is a moiety of formula (II):



wherein

A and B are defined as in any of claims 1 to 13;

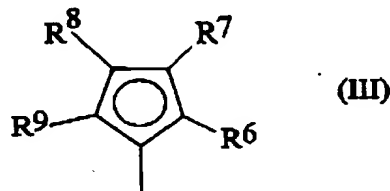
R^3 and R^4 , same or different from each other, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom, which can form a ring having 3 to 8 atoms which can bear a substituent;

G is a moiety as defined in any of claims 1 to 13;

and

(B) an alumoxane and/or a compound capable of forming an alkyl metallocene cation.

37. The process according to claim 36, wherein in the metallocene of formula (I) the transition metal M is selected from titanium, zirconium and hafnium.
38. The process according to any of claims 36 to 37, wherein in the metallocene of formula (I) the X substituents are chlorine atoms or methyl groups.
39. The process according to any of claims 36 to 38, wherein in the metallocene of formula (I) one of A is a sulfur atom and the other is a CH group and R^3 , which is the same to R^4 , is selected from hydrogen and an C_1 - C_{20} -alkyl group, which can contain a silicon atom.
40. The process according to claim 39, wherein in the metallocene of formula (I) R^3 and R^4 are a methyl or a trimethylsilyl radical.
41. The process according to any of claims 36 to 40, wherein in the metallocene of formula (I) the bridging group L is $=CMe_2$ or $=SiMe_2$.
42. The process according to claim 36, wherein in the metallocene of formula (I) G is a moiety of formula (III):



wherein

R^6 and R^9 , same or different from each other, are selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing a heteroatom,

R^7 is selected from a C_6-C_{20} -aryl, C_7-C_{20} -alkylaryl or a $QR^{11}R^{12}R^{13}$ group, wherein Q is selected from C, Si, Ge,

R^{11} , R^{12} and R^{13} , same or different from each other, are hydrogen, C_1-C_{20} -alkyl, C_3-C_{20} -cycloalkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, C_7-C_{20} -alkylaryl, C_7-C_{20} -arylalkyl radicals, optionally containing a heteroatom, with the proviso that when Q is a carbon atom, at least one of R^{11} , R^{12} and R^{13} is a hydrogen atom; and

R^8 is hydrogen.

43. The process according to claim 42, wherein in the metallocene of formula (I) R^7 is selected from phenyl, a $CHR^{11}R^{12}$ and a $SiR^{11}R^{12}R^{13}$ group, wherein R^{11} , R^{12} and R^{13} are hydrogen or C_1-C_{20} -alkyl groups.
44. The process according to claim 43, wherein in the metallocene of formula (I) $QR^{11}R^{12}R^{13}$ is an isopropyl or a trimethylsilyl group.
45. The process according to any of claims 36 to 44, wherein the metallocene of formula (I) is

isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 dimethylsilyl(3-trimethylsilyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(2-methyl-4-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(3-isopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride;
 isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;
 isopropylidene(3-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(2-methyl-4-phenyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

dimethylsilandiyl(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

isopropylidene(3-isopropylcyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and

isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)hafnium dichloride.

46. The process according to claim 36, wherein in the metallocenes of formula (I) G is a moiety of formula (IV) as defined in any of claims 11 to 13.
47. The process according to claim 36 for the preparation of homo- and copolymers of propylene.
48. The process according to claim 47, wherein the process is carried out in the presence of an alpha-olefin selected from 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene and 1-dodecene.
49. The process according to claim 36, wherein said process is carried out at a temperature comprised between -100 and +100°C and at a pressure comprised between 0,5 and 100 bar.
50. A propylene copolymer containing from 0.1 to 20% by moles of units deriving from an olefin of formula $\text{CH}_2=\text{CHR}$, R being hydrogen, a $\text{C}_2\text{-C}_{20}$ -alkyl or a $\text{C}_6\text{-C}_{12}$ -aryl group, said propylene copolymer having the following characteristics:
 - melting enthalpy < 70 J/g;
 - triads (mm) satisfy the relation: $30 < \text{mm} < 85$.
51. The propylene copolymer according to claim 50 wherein the olefin of formula $\text{CH}_2=\text{CHR}$ is ethylene.
52. Use of a propylene polymer optionally containing from 0.1 to 20% by moles of units

(TC5420.EP)

deriving from an olefin of formula $\text{CH}_2=\text{CHR}$, R being hydrogen, a $\text{C}_2\text{-C}_{20}$ -alkyl or a $\text{C}_6\text{-C}_{12}$ -aryl group, said propylene polymer having the following characteristics:

- melting enthalpy $< 70 \text{ J/g}$;
- $30 < \text{isotactic triads (mm)} < 85$,

for the preparation of synthetic leather, roofing blends, geomembranes, transparent objects, foamed beds, as additive for bitumen or as polymer support for pigments and/or colors in masterbatches.

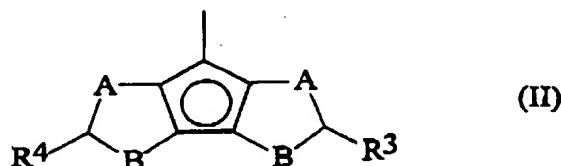
53. The use of a propylene polymer according to claim 52, wherein said propylene polymer has intrinsic viscosity values $[\eta]$ of greater than 0.5.
54. The use of a propylene polymer according to any of claims 53 and 54, wherein in said propylene polymer the isotactic triads (mm) satisfy the relation $40 < \text{isotactic triads (mm)} < 80$.

ABSTRACT:

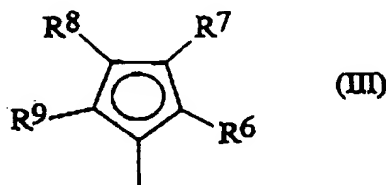
It is disclosed metallocene compounds of the general formula (I):

LGZMX_p (I)

wherein L is a divalent group, Z is a moiety of formula (II):



wherein R³ and R⁴ are selected from hydrogen and hydrocarbon groups; at least one of R³ and R⁴ being different from hydrogen; A and B are selected from S, O or CR⁵, wherein R⁵ is selected from hydrogen and hydrocarbon groups, either A or B being different from CR⁵; G is a moiety of formula (III):



wherein R⁶, R⁷, R⁸ and R⁹ are selected from hydrogen and hydrocarbon groups, and R⁶ and R⁷ and/or R⁸ and R⁹ can form a ring comprising from 3 to 8 atoms, which can bear substituents, with the provisos that R⁷ is different from R⁸ and when R⁷ is a tert-butyl radical, R⁸ is not hydrogen; M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements (new IUPAC version), X is selected from a halogen atom, a R¹⁰, OR¹⁰, OSO₂CF₃, OCOR¹⁰, SR¹⁰, NR¹⁰, or PR¹⁰, group, wherein the substituents R¹⁰ is hydrogen and a hydrocarbon group; p is an integer of from 0 to 3, being equal to the oxidation state of the metal M minus 2. Metallocenes of the above type are particularly useful for the preparation of polypropylene with a low degree of crystallinity.

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